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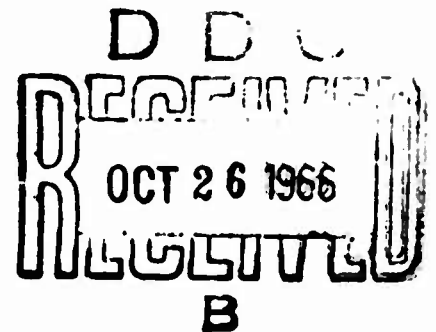afml ltr, 7 dec 1972

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HIGH STRENGTH - HIGH MODULUS GLASS FIBERS

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OWENS-CORNING FIBERGLAS CORPORATION

TECHNICAL REPORT AFML-TR-65-90, Part II

July 1966

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This technical report has been reviewed and is approved.

J. A. Ross

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ABSTRACT

The purpose of this investigation has been the study of glass compositions capable of producing glass fibers having high tensile strength-high modulus of elasticity properties which are also low in density. Of the many compositions studied, those which have the best promise of meeting the required properties are located in the SiO_2-Al_2O_3-BeO system. In particular, compositions have been developed in this system with tensile strengths of 680-715,000 psi, moduli of 14- 15×10^6 psi, and bulk densities of 2.41-2.50. These properties produce fibers with specific strengths and specific moduli in excess of any currently available glass fiber. Successful multifilament manufacture of glasses of this nature was demonstrated and unidirectional filament wound composites were fabricated and tested. In a basic study aimed at relating glass properties, composition, and structure, three and four component systems were studied consisting of SiO_2 and Al_2O_3 plus one of the following: K_2O, Li_2O, $K_2O + Li_2O$, MgO, CaO, ZnO and BeO. For glasses containing K_2O, Li_2O, $K_2O + Li_2O$, or CaO, curves of modulus vs. the ratio of aluminum to added ion showed breaks at the point where one oxygen ion had been added per two aluminum ions. This was related to a proposed glass structure involving a change of coordination number of aluminum from four to six, with a corresponding change in the function of this ion in the structure. BeO, MgO and ZnO were similar to each other in behavior, but differed from the other oxides. They showed breaks in composition vs. modulus curves at different points than the other oxides, with the inflection point changing with SiO_2 content. These oxides increased modulus in the following order (BeO highest): BeO, MgO, ZnO, CaO, Li_2O, Na_2O, K_2O.

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SECTION I

INTRODUCTION

This present study is a continuation of the work reported in Technical Report AFML-TR-65-90, Part I, High Strength-High Modulus Glass Fibers[1]. Its purpose has been the preparation and study of glass compositions capable of producing glass fibers with high tensile strengths and high moduli of elasticity. An additional study was also continued which has sought to establish a relationship between tensile strength, modulus of elasticity, and the composition and probable constitution of selected glasses. Results of this additional study are presented in the section on "Relationship Between Composition and Properties of Selected Glasses."

In the study of high strength- high modulus glass fibers, emphasis was placed on glass compositions in the $SiO_2-Al_2O_3-BeO$, $SiO_2-Al_2O_3-MgO$, $SiO_2-Al_2O_3-ZnO$, and $SiO_2-Al_2O_3-Li_2O$ systems. Subsequent studies were made by adding various oxides to these base systems.

In the study of the relationship between composition and properties of glass, the systems studied contained SiO_2 and Al_2O_3 plus one of the following: K_2O, Li_2O, $K_2O + Li_2O$, MgO, CaO, ZnO and BeO. This represents a continuation of the initial work in which the $SiO_2-Al_2O_3-Na_2O$ system was studied.

SECTION II

Study of High Tensile Strength-High Modulus Glass Fiber Compositions

1. Glass Preparation, Fiberization, and Testing

Each glass composition was prepared by dry mixing the appropriate oxides, which were of at least U.S.P. grade, in a double-cone agitator wheel blender for approximately ten minutes. The dry batch was melted in precious metal crucibles. The melting temperatures utilized ranged from 2900°F to 3200°F; each glass was held at temperature for periods ranging from 2 to 24 hours. All glasses were cooled by plunging the hot crucible directly from the furnace into a water bath. Fibers were obtained from the glass compositions by remelting the prepared cullet in a one-hole precious metal bushing capable of reaching temperatures in excess of 3200°F.

To test the fibers, virgin filaments were captured by hand in the usual manner and, to determine the tensile strength, were wound on a stainless steel "fork" or holder. Each fork normally contained 6 to 8 fiber lengths for study after this operation. The apparatus for measuring tensile strength is designed to test one

fiber at a time, recording essentially the load elongation diagram of each fiber. The fibers are loaded by a screw-driven crosshead at a constant rate of strain of 0.25 in/in./minute over a gage length of two inches. The load cell consists of a centilever beam with a linear variable differential transformer (LVDT) as the displacement sensing element. The load cell is calibrated by dead-weight loading. The LVDT is powered by a strain gage amplifier. The signals from the LVDT are first rectified through matched pairs of germanium diodes, then passed through gain and zero potentiometers and recorded on a single channel Esterline-Angus recorder. A photograph of the apparatus is shown in Figure 1.

The fiber diameter of each fiber length (6-8) was determined from a short length of fiber remaining on the fork after a sample was mounted on the tensile strength apparatus. These short fiber lengths were mounted on a microscope slide in a liquid of appropriate index of refraction. The fiber diameters were measured under a 430 power microscope using a Vickers Image-Splitting Eyepiece.*

The measurement of tensile strength was considered, in this study, to be of primary importance. Care was taken, therefore, to obtain values which were representative of an optimized fiberization operation. The modulus of elasticity measurements were considered of secondary importance, except for glasses which showed promise of also having good tensile strength and density values.

The modulus of elasticity of a particular glass composition was determined by direct measurement of the elongation of an unannealed fiber under load. A photograph of the apparatus is shown in Figure 2.

Two fibers were utilized for the measurement. The sample diameter normally ranged from 0.00025- 0.00040 inches. To prevent fiber breakage under elongation only 1-5 gram weights could be used. All these factors(low sample numbers, small sample diameters, and low load application)produced modulus values which are less accurate than values described in Section III of this report titled "Relationship Between Composition and Properties of Selected Glasses." Indications are that the values are too low rather than too high under the test conditions described.

The bulk density of a glass sample was determined by the Archimedes method, using a piece of cullet weighing 5-7 grams which was essentially seed-free.

2.   Tensile Strength and Modulus of Elasticity Results

    a. SiO_2-Al_2O_3-ZnO System

       Of those glass systems studied under the first year's program,

*Supplied by Cooke, Troughton and Simms, Inc., Massachusetts
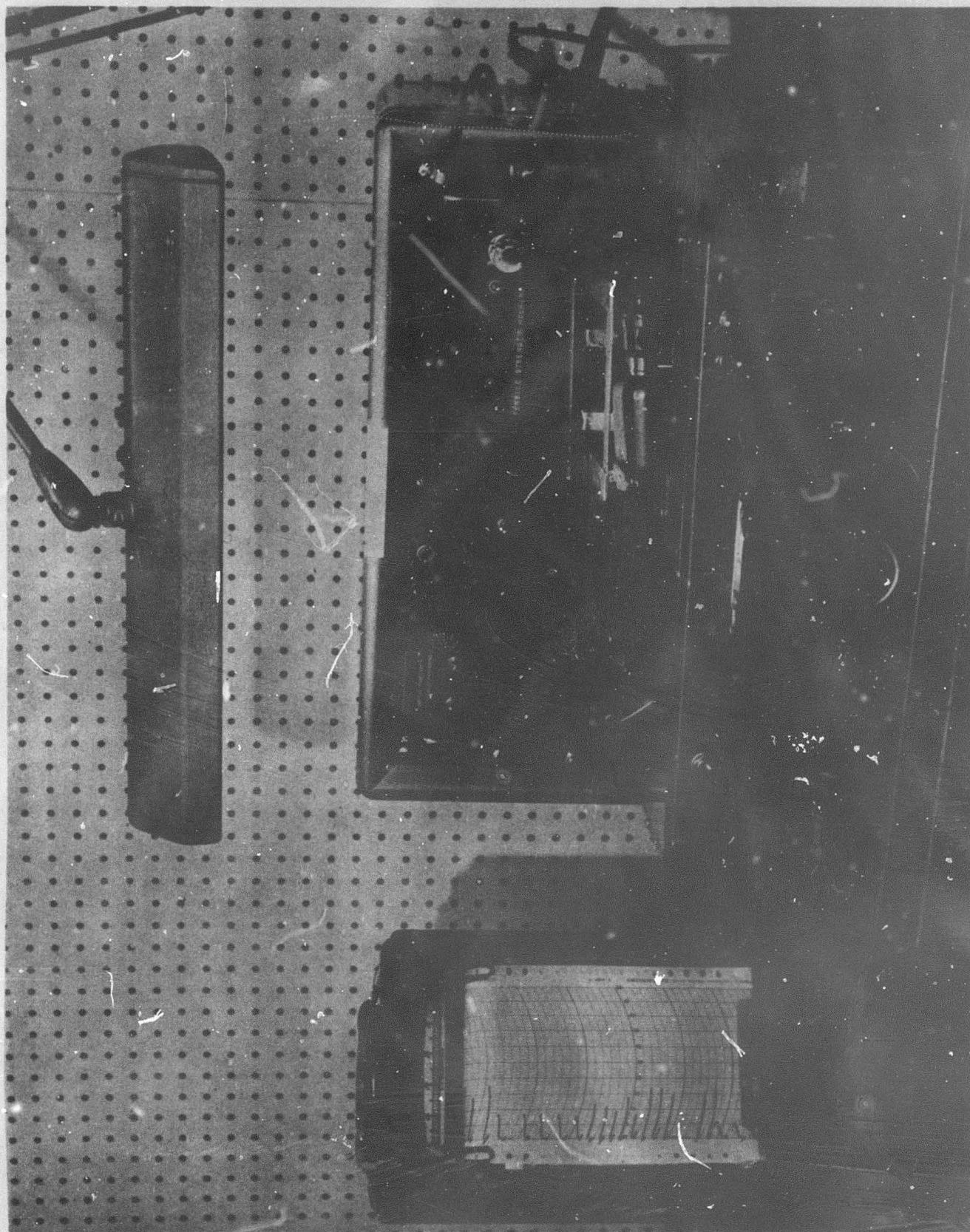
Figure 1 Tensile Strength Apparatus

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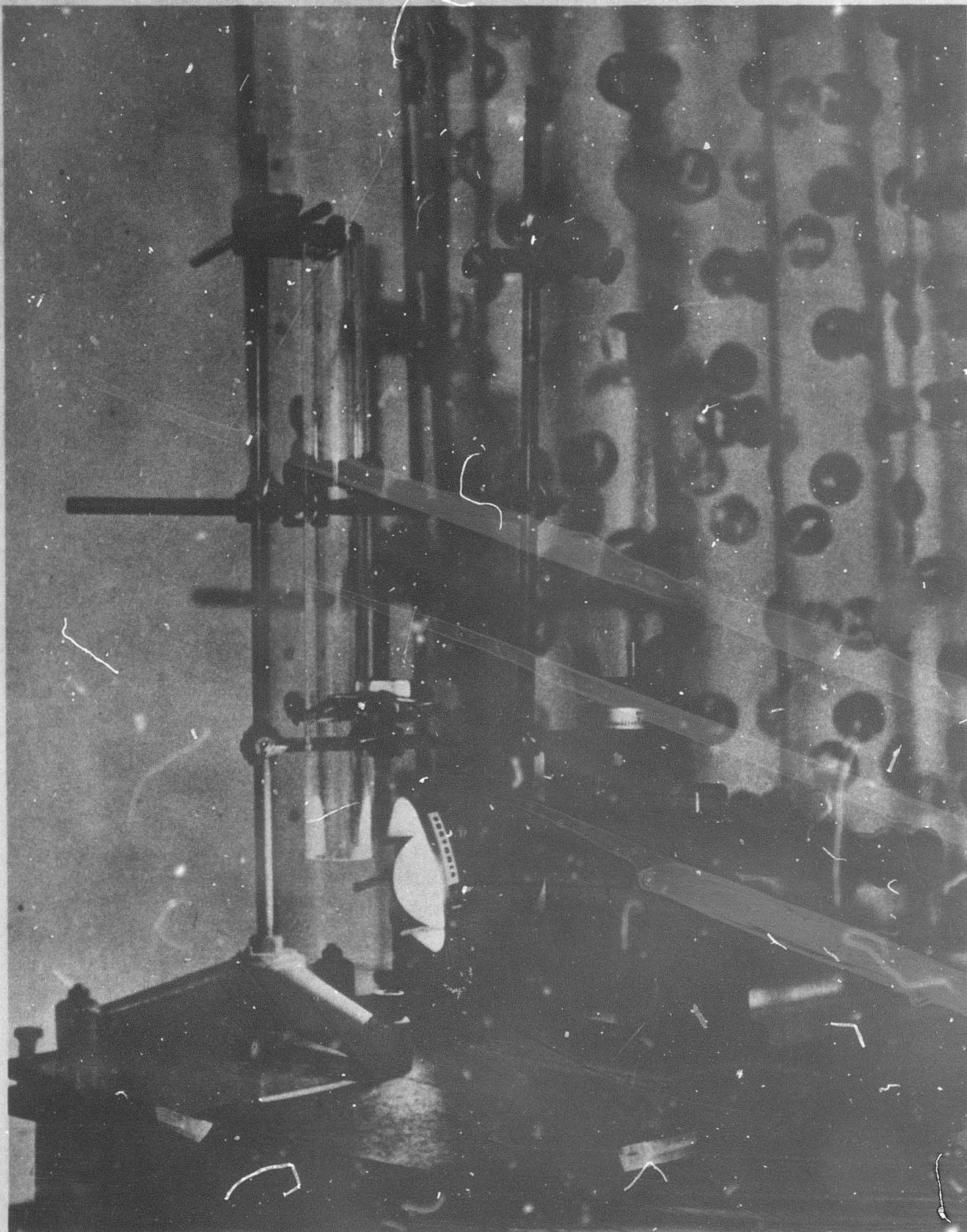
Figure 2 Modulus of Elasticity Apparatus

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one of the most promising was the SiO_2-Al_2O_3-ZnO system. The system contains glass X-1792-2, which was previously reported to have a tensile strength in excess of 800,000 psi. More extensive studies of SiO_2-Al_2O_3-ZnO glasses were therefore carried out. Those compositions studied are shown in Table I. Various properties for each composition are also shown in Table I. Also see Figure 3, a diagram of the SiO_2-Al_2O_3-ZnO system showing the location of all three component glasses studied in the system.

Previous work with this system indicated that the best tensile strength properties could be found with glasses having Al_2O_3 to ZnO mole ratios of 1.0. Eight compositions with variable SiO_2 contents were therefore selected at this mole ratio. Four others were selected at a le ratio of 0.5. Two were selected at mole ratios to either de of 1.0. A small amount of MgO was also added to one final composition.

The eight glasses represented by X-2034 through X-2041 (Al_2O_3 to ZnO mole ratio equals 1.0) demonstrate the effect of variations in SiO_2 content on the tensile strength of the final glass fiber. As indicated by the results in Table I, the tensile strength increases from 60-68 mole percent SiO_2 and then decreases slowly from 68-80 mole percent SiO_2. In the same series the modulus has decreased continuously from 60-80 mole percent SiO_2. The bulk density has also decreased continuously over the same range of values. The tensile strength, therefore, is a maximum at a point approximately midway between the minimum and maximum modulus and midway between the maximum and minimum bulk density. This has proved to be the case in all of the other three-component systems investigated. It appears then that no one glass in a system can possess the highest tensile strength, the highest modulus, and the lowest density of all glasses in the system.

The four glasses represented by X-2043 through X-2046 (Al_2O_3 to ZnO mole ratio of 0.5) demonstrate the effect on tensile strength of a reduction in the ratio of Al_2O_3 to ZnO. The increase in the ZnO content reduces the strength, at these SiO_2 levels, and increases the modulus and density. Glasses with an Al_2O_3 to ZnO mole ratio slightly below 1.0 (see X-2042) show similar reactions with respect to the tensile strength and density.

Glasses with Al_2O_3 to ZnO mole ratios slightly greater than 1.0 (X-2060) produce no great modulus improvement and no strength improvement. Al_2O_3 to ZnO mole ratios greater than 1.13 (X-2060) were not studied because of the expected increases in forming temperature and decreases in tensile strength. The relationship

TABLE I

SiO_2 - Al_2O_3 - ZnO System and Modifications

Glass No.	Oxides (a. weight %, b. mole %)						Average Tensile Strength $\times 10^3$ psi	Modulus of Elasticity $\times 10^6$ psi	Average Diameter $\times 10^{-5}$ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
	SiO_2	Al_2O_3	MgO	ZnO	BeO	Li_2O						
X-2034 a.	44.5	30.9		24.6			Could not be fiberized					
b.	55.0	22.5		22.5								
X-2035 a.	49.57	28.05		22.38			573	11.7	32	2880	17	2.8
b.	60.0	20.0		20.0								
X-2036 a.	54.9	25.1		20.0			560	11.6	37	2850	14	2.8
b.	65.0	17.5		17.5								
X-2037 a.	58.2	23.2		18.6			706	11.6	30	2955	9	2.7
b.	68.0	16.0		16.0								
X-2038 a.	60.46	21.99		17.55			619	11.5	22	2945	17	2.7
b.	70.0	15.0		15.0								
X-2039 a.	62.8	20.7		16.5			648	10.8	33	2995	15	2.6
b.	72.0	14.0		14.0								
X-2040 a.	66.29	18.75		14.96			515	11.4	34	3025	16	2.7
b.	75.0	12.5		12.5								
X-2041 a.	72.39	15.36		12.26			523	11.3	28	3075	16	2.5
b.	80.0	10.0		10.0								

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TABLE I (Continued)

Glass No.	SiO$_2$	Al$_2$O$_3$	MgO	ZnO	BeO	Li$_2$O	Average Tensile Strength x10^3 psi	Modulus of Elasticity x10^6 psi	Average Diameter x10^{-5} in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2042	60.8	19.2		20.0			394	11.2	37	2850	16	2.78
	70.0	13.0		17.0								
X-2043	40.5	22.9		36.6			Could not be fiberized					
	50.0	16.7		33.3								
X-2044	50.5	19.1		30.4			557	12.2	29	2715	18	2.9
	60.0	13.3		26.7								
X-2045	53.2	18.0		28.8			314	12.8	30	2700	16	2.9
	62.5	12.5		25.0								
X-2046	61.37	14.88		23.75			468	11.3	44	2900	14	2.8
	70.0	10.0		20.0								
X-2060	58.04	24.62		17.34			488	11.9	36	2850	18	2.6
	68.0	17.0		15.0								
X-2324	62.7	20.8	5.5	11.1			690	12.4	34	2900	15	2.63
	68.68	13.42	8.95	8.95								
X-1792-2 (previously reported)	59.0	22.7		18.3			815	11.5	26	2915	11	2.7
	68.68	15.56		15.76								

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FIGURE 3

$SiO_2 - Al_2O_3 - ZnO$ SYSTEM
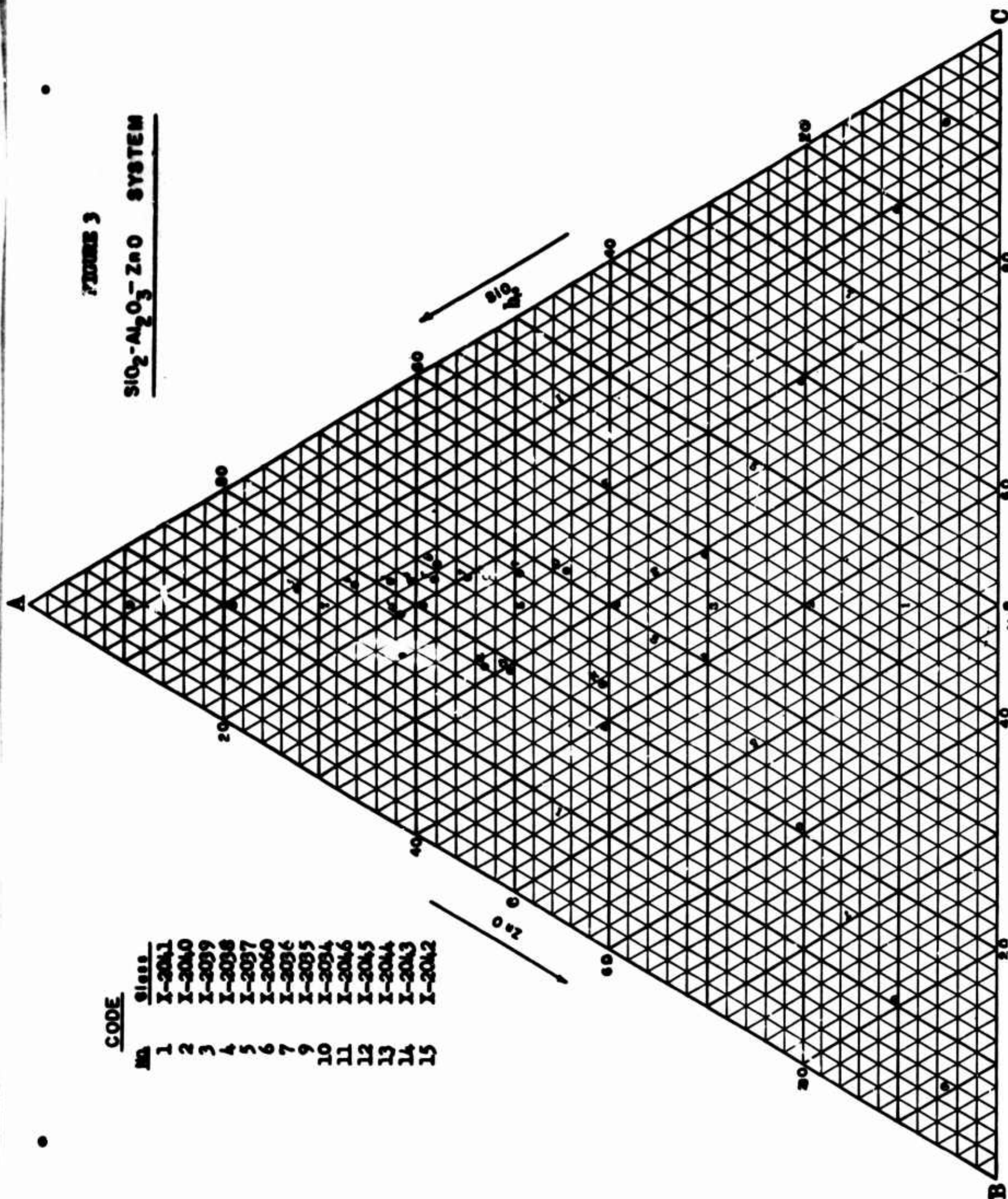
CODE

No	Glass
1	I-2041
2	I-2040
3	I-2039
4	I-2038
5	I-2037
6	I-2050
7	I-2036
9	I-2035
10	I-2034
11	I-2046
12	I-2045
13	I-2044
14	I-2043
15	I-2042

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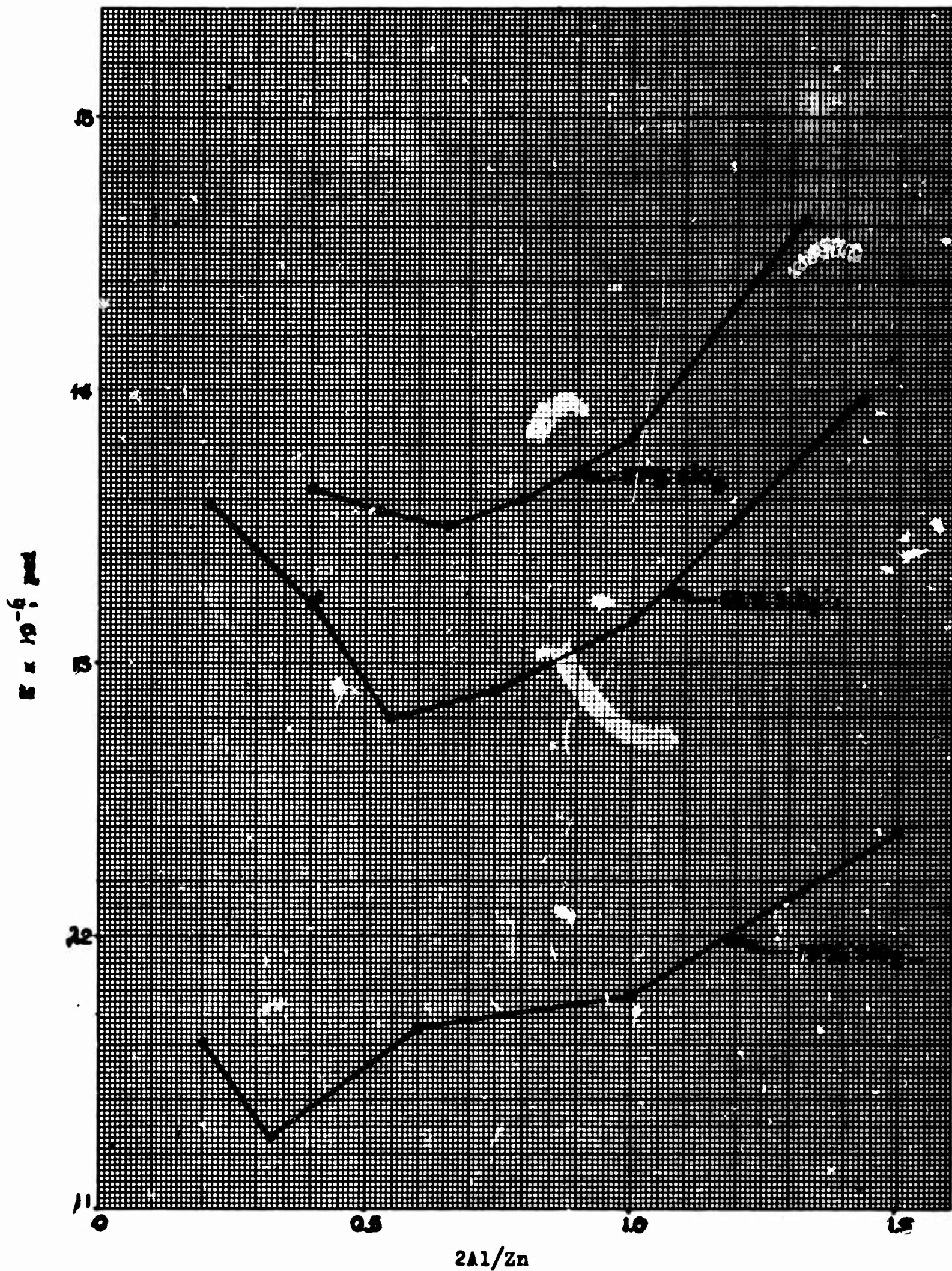
Figure 4   Modulus Vs. 2 Al/Zn Ratio

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between modulus and Al_2O_3 to ZnO mole ratio are more clearly shown in the study, "Relationship Between Composition and Properties of Selected Glasses" (See Figure 4). The primary problem with glasses in the SiO_2-Al_2O_3-ZnO system, some of which have tensile strength properties equal to or greater than S-994, is the fact that the densities are greater than 2.5 g/cc. As shown by X-2324, a modification of X-1792-2 containing MgO, both the modulus and density values can be improved by the proper addition of an appropriate oxide. Strength is sacrificed, however, and the density still does not drop below 2.5 g/cc.

To determine some of the problems which might be expected with a glass of the SiO_2-Al_2O_3-ZnO type, a multifilament trial of X-1792-2 was made. A standard 204-hole production-type bushing was utilized and an initial run of 20 hours was made. Bushing capacity and design were such that, after 10 hours, devitrification had begun to interefere with the fiberization process. Nevertheless, three sample forks of tensile strength fibers were obtained five hours after the run started. The strength, an average of 21 separate breaks, was 635,000 psi. This was considered to be excellent in light of the fact that strength optimization in a multifilament operation requires at least 24 hours of continuous, uninterrupted operation.

No problems were seen that would prevent eventual continuous multifilament fiberization of X-1792-2. Proper selection of a standard 204-hole production bushing, keeping in mind the higher forming temperature, higher density, and increased devitrification tendencies of this glass, would be the only major consideration required.

b. SiO_2-Al_2O_3-BaO System
_____

Another promising glass system studied during the course of the year's program was the SiO_2-Al_2O_3-BeO system. More extensive studies of this system were therefore made. These initially dealt with glasses having Al_2O_3 to BeO mole ratios of 1.0 or 0.5 and variable mole percentages of SiO_2. The composition and properties of these glasses are shown in Table II titled "SiO_2-Al_2O_3-BeO System and Modifications" (see X-2047 to X-2055). Figure 5 shows the location of these and the remaining three-component glasses studied in the system.

At an Al_2O_3 to BeO mole ratio of 1.0, as indicated by the results for X-2047 through X-2051, the fiber tensile strength increases from 60 to 70 mole percent SiO_2 and then decreases from 70 to 80 mole percent SiO_2. Over the same range of values the modulus and the bulk density decrease continuously. Maximum tensile strength and modulus with minimum density are therefore not found in any one glass.

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TABLE II

SiO_2 - Al_2O_3 - BeO System and Modifications

Glass No.	Oxides (a. weight %, b. mole %)					Average Tensile Strength $\times 10^3$ psi	Modulus of Elasticity $\times 10^6$ psi	Average Diameter $\times 10^{-5}$ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
	SiO_2	Al_2O_3	MgO	BeO	Li_2O						
X-2047 a.	58.67	33.19		8.14		Could not be fiberized					
b.	60.0	20.0		20.0							
X-2048	63.74	29.12		7.14		522	13.7	43	3040	16	2.48
	65.0	17.5		17.5							
X-2049	69.1	25.1		5.8		742	12.0	28	3040	15	2.43
	70.0	15.0		15.0							
X-2050	74.0	20.9		5.1		700	12.2	35	3075	18	2.35
	75.0	12.5		12.5							
X-2051	79.1	16.8		4.1		561	11.1	25	3050	17	2.3
	80.0	10.0		10.0							
X-2052	64.02	24.14		11.84		449	12.6	49	2915	16	2.5
	60.0	13.3		26.7							
X-2053	68.78	20.96		10.27		418	11.9	40	2945	18	2.44
	65.0	11.7		23.2							
X-2054	73.46	17.81		8.73		607	11.5	36	3050	17	2.44
	70.0	10.0		20.0							
X-2055	78.1	14.7		7.2		478	12.2	32	3075	16	2.35
	75.0	8.3		16.7							

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TABLE II (Continued)

Glass No.	SiO_2	Al_2O_3	MgO	BeO	Li_2O	Average Tensile Strength x 10³ psi	Modulus of Elasticity x 10⁶ psi	Average Diameter x 10⁻⁵ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2056	47.2 50.0	40.0 25.0	7.9 12.5	4.9 12.5		Could not be fiberized					
X-2057	57.25 60.0	32.39 20.0	6.40 10.0	3.97 10.0		Could not be fiberized					
X-2058	67.56 70.0	24.57 15.0	4.85 7.5	3.01 7.5		614	11.4	33	2915	15	2.47
X-2059	78.1 80.0	16.6 10.0	3.3 5.0	2.0 5.0		600	11.0	25	3050	15	2.3
X-2061	67.2 70.0	24.4 15.0	6.4 10.0	2.0 5.0		739	12.9	20	2915	16	2.5
X-2062	66.7 70.0	24.3 15.0	8.0 12.5	1.0 2.5		510	12.4	35	2915	16	2.5
X-2063	68.4 70.0	24.9 15.0		3.1 7.5	3.6 7.5	757	11.7	14	2915	15	2.41
X-2064	67.4 70.0	24.5 15.0	4.8 7.5	1.5 3.75	1.8 3.75	776	12.2	19	3060	17	2.38
X-2065	67.99 70.0	24.73 15.0	2.44 3.75	3.03 7.5	1.81 3.75	653	11.7	30	2975	18	2.41
X-2124	71.1 70.0	21.5 12.5		7.4 17.5		681	14.1	31	2850-2915	15	2.41

TABLE II (Continued)

Glass No.	SiO$_2$	Al$_2$O$_3$	MgO	ZnO	BeO	Li$_2$O	Average Tensile Strength x 10^3 psi	Modulus of Elasticity x 10^6 psi	Average Diameter x 10^{-5} in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2125	61.9 / 65.0	28.3 / 17.5	7.5 / 11.7		2.3 / 5.8		841	13.3	20	2850	15	2.5
X-2126	67.1 / 70.0	27.7 / 17.0			5.2 / 13.0		778	14.1	32	3040	15	2.45
X-2127	61.9 / 65.0	32.1 / 19.8			6.0 / 15.2		655	13.6	37	3100	15	2.52
X-2128	62.4 / 64.0	29.8 / 18.0			4.9 / 12.0	2.9 / 6.0	643	13.0	27	2915	16	2.45
X-2129	62.2 / 65.0	28.4 / 17.5	5.6 / 8.75		1.7 / 4.38	2.1 / 4.38	764	13.3	24	2850	15	2.47
X-2132	57.0 / 60.0	32.3 / 20.0	6.4 / 10.0		2.0 / 5.0	2.4 / 5.0	590	13.4	38	2850	15	2.55
X-2167	66.2 / 65.0	25.2 / 14.6			8.6 / 20.4		537	14.2	27	2900	15	2.40
X-2168	59.4 / 60.0	29.4 / 17.5	5.0 / 7.5		6.2 / 15.0		421	15.7	36	2850	10	2.55
X-2170	61.6 / 65.0	28.2 / 17.5	1.8 / 2.9	3.7 / 2.9	4.6 / 11.7		712	12.9	26	2955	15	2.55
X-2171	60.6 / 65.0	27.6 / 17.5		7.3 / 5.8	4.5 / 11.7		694	14.3	34	2955	17	2.6

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TABLE II (Continued)

Glass No.	SiO$_2$	Al$_2$O$_3$	MgO	ZnO	BeO	Li$_2$O	Average Tensile Strength x10^3 psi	Modulus of Elasticity x10^6 psi	Average Diameter x10^{-5} in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2252	73.0	20.0			7.0		500	13.3	34	2975	15	2.4
	71.8	11.6			16.6							
X-2253	71.0	20.5			8.5		702	13.8	29	2965	15	2.4
	68.6	11.7			19.7							
X-2254	71.0	22.5			6.5		452	11.5	28	2955	5	2.4
	71.1	13.3			15.6							
X-2255	69.0	23.0			8.0		473	12.2	39	2975	17	2.5
	67.8	13.3			18.9							
X-2256	68.0	22.5			9.5		521	12.3	35	3040	15	2.6
	65.3	12.7			21.9							
X-2257	68.0	24.5			7.5		651	13.5	34	2965	15	2.3
	67.7	14.4			17.9							
X-2258	67.0	24.5			8.5		422	13.7	45	2975	15	2.4
	65.8	14.2			20.1							
X-2259	65.0	26.0			9.0		439	12.9	48	2850	15	2.5
	63.8	15.0			21.2							
X-2260	62.5	28.0			9.5		633	13.9	21	2880	17	2.5
	61.4	16.2			22.4							
X-2261	74.0	22.0			4.0		754	12.8	19	3095	15	2.4
	76.6	13.4			10.0							

TABLE II (Continued)

Glass No.	SiO₂	Al₂O₃	MgO	ZnO	BeO	ZrO₂	Average Tensile Strength x10³ psi	Modulus of Elasticity x10⁶ psi	Average Diameter x10⁻⁵ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2275	72.0	20.8			7.2		416	12.6	40	3040	16	2.4
	70.9	12.1			17.0							
X-2276	70.0	22.4			7.6		542	13.5	36	2915	15	2.4
	68.9	13.0			18.1							
X-2277	71.0	21.0			8.0		511	12.6	46	3040	14	2.4
	69.2	12.1			18.7							
X-2278	71.0	22.0			7.0		481	13.3	39	2915	15	2.45
	70.4	12.9			16.7							
X-2279	69.62	21.10			7.24	2.04	477	13.9	37	2915	15	2.4
	69.31	12.38			17.33	0.99						
X-2280	68.2	30.7			7.1	4.0	544	13.1	35	2915	15	2.5
	68.63	12.25			17.16	1.96						
X-2281	66.9	20.3			6.9	5.9	670	14.4	41	2950	15	2.5
	68.3	12.1			17.0	2.9						
X-2282	68.3	20.7		3.9	7.1		476	13.6	35	2915	15	2.5
	68.0	12.1		2.9	17.0							
X-2283	66.5	20.2		6.4	6.9		422	12.8	31	2915	15	2.5
	66.69	11.93		4.74	16.64							
X-2284	69.3	21.0	1.3		8.4		518	13.8	32	2845	15	2.4
	68.63	12.25	1.96		17.16							

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TABLE II (Continued)

Glass No.	SiO_2	Al_2O_3	MgO	BeO	CeO_2	ZrO_2	Average Tensile Strength $x 10^3$ psi	Modulus of Elasticity $x 10^6$ psi	Average Diameter $x 10^{-5}$ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2285	69.1 67.31	21.0 12.02	2.7 3.85	7.2 16.83			715	14.95	25	2915	15	2.5
X-2320	69.71 69.5	21.08 12.4		7.25 17.4	1.96 0.7		545	13.6	27	2915	14	2.5
X-2321	68.4 69.2	20.7 12.3		7.1 17.2	3.8 1.3		565	14.3	27	2915	15	2.5

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FIGURE 5

SiO_2-Al_2O_3-BeO SYSTEM

(the large diagram is a detail of the area within the dotted lines)

CODE

No.	Glass		No.	Glass
1	X-2055		17	X-2167
2	X-2054		18	X-2259
3	X-2053		19	X-2260
4	X-2052		20	X-2051
5	X-2252		21	X-2050
6	X-2275		22	X-2049
7	X-2253		23	X-2048
8	X-2124		24	X-2261
9	X-2124		25	X-2126
10	X-2278		26	X-2127
11	X-2254			
12	X-2276			
13	X-2255			
14	X-2256			
15	X-2257			
16	X-2258			
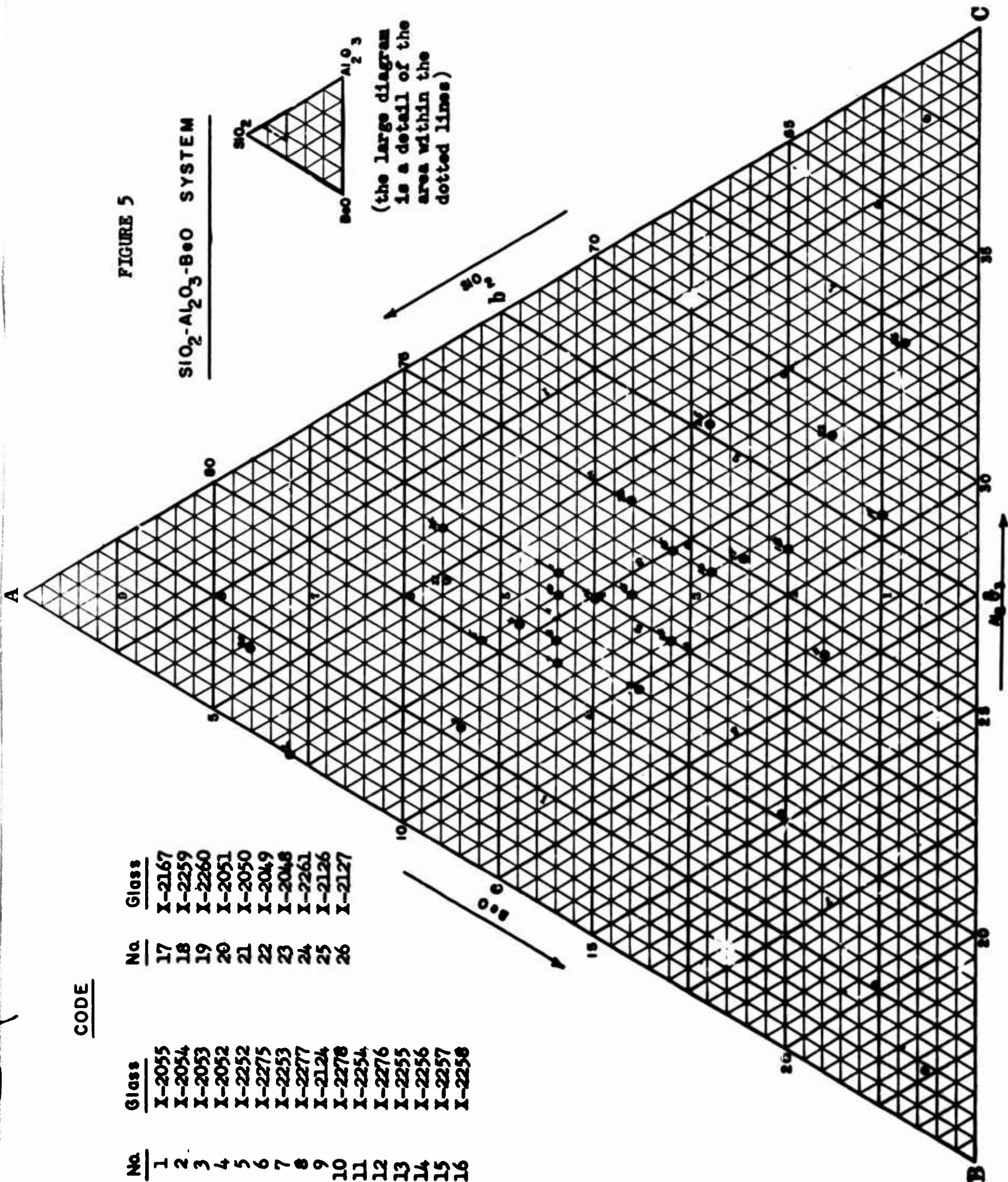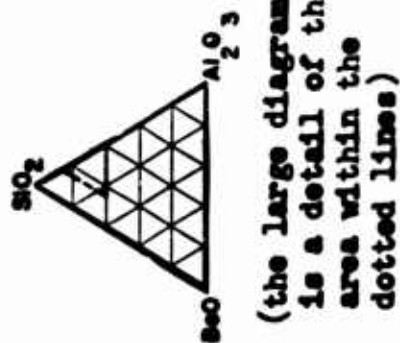
X-2052 through X-2055, with Al_2O_3 to BeO mole ratios of 0.5, show a similar peak in strength at 70 mole percent SiO_2. In general, both the modulus and density decrease over the range of 60 to 75 mole percent SiO_2. The tensile strength and modulus properties of this series are lower than those for the X-2047 to X-2051 series, however.

A major problem encountered with the glasses previously discussed is their high forming temperatures. As seen in Table II, these are greater than $3000^\circ F$ for all but two glasses. MgO and/or Li_2O were therefore added in various combinations both to lower forming temperature and to determine their effects on fiber strength, modulus and density. In Table II these glasses are designated X-2056 through X-2059 and X-2061 through X-2065.

The Al_2O_3 to BeO + R_xO mole ratio for each glass was maintained at 1.0. X-2056 through X-2059, with MgO substituted for half the BeO, show a reduction in strength and modulus. Below 70 mole percent SiO_2 the glass could not be fiberized. Additions of unequal proportions of R_xO and BeO were more successful, as shown by several glasses in the X-2061 to X-2065 series. Note that X-2061, X-2063, and X-2064 have strengths well in excess of 700,000 psi. X-2061 and X-2063 have more acceptable forming temperatures. As for the modulus of elasticity values for these three glasses, they should be related to the density of each glass. Since all three have lower densities than AF-994 for example, their specific moduli are greater than AF-994.

These modifications of the basic three-component system, SiO_2-Al_2O_3-BeO, were further modified to try to increase modulus of elasticity. X-2125 and X-2168 were melted and tested on the basis of results previously obtained for X-2058, X-2061 and X-2062. X-2125 and X-2168 have less SiO_2 and more Al_2O_3 on a mole basis; as expected, their moduli are higher than the compositions on which they are based. The high tensile strength of X-2125 is attributed to the high Al_2O_3 content and optimum Al_2O_3 to RO mole ratio. The modulus of X-2168 is attributed to its high BeO content.

X-2170 and X-2171 are modifications of X-2125 containing ZnO. In the case of X-2171 the ZnO addition apparently improved the modulus materially. However, it also produced an immediate increase in the bulk density.

X-2128, a modification based on X-2063, has a lower SiO_2 content and a change in the ratio of BeO to Li_2O. As expected, when the SiO_2 content is lowered, the modulus of X-2128 improves above that of X-2063, but its tensile strength drops. The density has also increased slightly.

Finally, X-2129 and X-2132 were based on X-2064 and have a lower SiO_2 content with changes in the various ratios between

Al_2O_3, MgO, Li_2O, and BeO. As expected, the lower SiO_2 content improved the modulus and increased the density. In the case of X-2129, the final tensile strength was not impaired by these changes when compared to X-2064.

In general, these modification studies have shown that MgO and/or Li_2O may be added to glasses in the SiO_2-Al_2O_3-BeO system in various combinations and they will improve fiberization properties and lower density. As the density is lowered within a given composition, however, the modulus also decreases. All of these effects seem to be tied to the SiO_2 content. The higher SiO_2 content glasses have improved strength, lower density, and lower modulus values. Lower SiO_2 contents produce higher moduli, higher densities, and lower strengths.

Such modification operations, however, have not substantially improved overall glass properties in this system. More intensive studies of the SiO_2-Al_2O_3-BeO system were therefore made in areas other than those associated with the Al_2O_3 to BeO mole ratio of 1.0 and 0.5. Initial objectives were to locate compositions with higher tensile strengths and/or lower forming temperatures.

These objectives led to fiberization of glasses designated X-2124, X-2167, X-2126, and X-2127. Note that the SiO_2 level for all four glasses falls between 65 and 70 mole percent, the area associated with fibers of the highest tensile strength. The first two compositions have an Al_2O_3 to BeO mole ratio of 0.71, while with the second two, Al_2O_3/BeO = 1.31.

Though the tensile strength of X-2126 is the best in this series, its forming temperature is above 3000°F. It appears that this is the case for all glasses with an Al_2O_3 to BeO mole ratio greater than 1.0. This is borne out by the other results (see the properties of X-2261, Al_2O_3/BeO = 1.34). The high forming temperatures are attributed to the increased Al_2O_3 content of these glasses.

X-2124 and X-2167 have much more desirable forming temperatures. Overall, X-2124 has the best properties, combining a high tensile strength, good modulus, and very low density. Virgin fiber samples of X-2124 were submitted to the Air Force Materials Laboratory for their evaluation. Their results are compared below to those originally reported by OCF.

AFML Results

T.S. = 643×10^3 psi

E = 14.7×10^6 psi

  (sonic method)

Fiber Diameter = 33.4×10^{-5} in.

OCF Results

T.S. = 681×10^3 psi

E = 14.1×10^6 psi

  (elongation method)

Fiber Diameter for E measurement = 56×10^{-5} in.

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These very interesting results led to extensive studies of the region in Figure 5 bounded by an imaginary line drawn through the points labeled 1,2,3,4 and an imaginary line drawn through 20, 21, 22, 23. This region is characterized by Al_2O_3 to BeO mole ratios ranging from 0.58 to 0.85 and SiO_2 mole percentages of 61.4 to 71.8. The glasses in this region were designated X-2252 through X-2260 and X-2275 through X-2278. Their compositions and properties may be found in Table II and their positions in relation to the X-2124 composition may be seen in Figure 5.

It was expected that the properties of these glasses would in several cases be more desirable than those associated with X-2124. However, both the tensile strength and modulus values for all the glasses were lower than expected. From data developed later in melting and forming temperature studies of X-2124, it was concluded that the two property values were low because the glasses were not melted under optimum conditions. All of the modified compositions were melted from batch at temperatures of $2900°F$ to $3200°F$ for periods of up to four hours.

The data mentioned earlier concerning melting and forming temperature studies of X-2124 is shown in Table III. It is evident that if X-2124 is melted under less than optimum conditions (assumed to be 24 hours at $2900°F$) its tensile strength and modulus properties will be similar to those of X-2252 through X-2260 and X-2275 through X-2278.

TABLE III

THE EFFECT OF THERMAL TREATMENT ON THE TENSILE STRENGTH AND MODULUS OF X-2124

BATCH MELTING TIME and TEMP.		FORMING TEMP. °F	FORMING TIME HR.	T.S. $\times 10^3$ psi	E $\times 10^6$ psi
4 Hr.	2900°F	2915	1/2	471	-
4	2900	2965	2	625	12.7
4	3200	2850	2	440	12.5
4	3200	2915	1	500	11.8
4*	3200	2915	1	500	14.3
4	3200	2975	3	540	-
8 Hr.	2900°F	2890	1	453	-
8	2900	2915	1/2	532	13.4
8	3200	2915	7	535	-
8	3200	2965	2	525	14.5
24 Hr.	2900°F	2900	5	700	12.4
24	2900	2915	3	681	14.1
24*	2900	2915	3	670	14.4
24	2900	2950	1	696	-

* Properties rechecked using a new batch of glass

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It is apparent that the melting conditions used for SiO_2-Al_2O_3-BeO type glasses influence properties to a great extent, probably much more than small composition modifications or additions.

Before the X-2124 melting history study was completed, several oxide additions were made to this composition to determine their effect on strength, modulus and density. The resultant glasses are represented by X-2279 through X-2285 and X-2320 through X-2321. X-2279 through X-2283 contain ZrO_2 or ZnO and were melted for four hours at 3200°F, melting conditions which are not optimum for glasses of the $SiO_2Al_2O_3$-BeO type. Therefore the tensile strengths are undoubtedly lower than could be obtained. The moduli of these glasses do not appear to have decreased as much as those for X-2124 melted under similar conditions. Their densities have increased, however, and would be expected to go higher with increasing oxide additions, thus preventing improved specific modulus values. Subsequent melts of these glasses at 2900°F for 24 hours definitely improved their properties. For instance, X-2281 melted under optimum conditions had an average tensile strength of 670,000 psi and an average modulus of 14.4×10^6. Earlier less optimum melts gave tensile strength properties of 582,000 psi and moduli of 13.6×10^6 psi. Glasses X-2253, X-2257, and X-2260 showed similar improvements when melted under optimum conditions with the best properties being reported in Table II.

Glasses X-2284 and X-2285 contain MgO while glasses X-2320 and X-2321 contain CeO_2. These glasses were melted at near optimum conditions, 2900°F for 23 hours. At least one of these, X-2285, had excellent properties. Though its bulk density has increased to 2.5, its modulus has also increased. The CeO_2 additions do not improve modulus and apparently lower the tensile strength. As expected, CeO_2 also increases bulk density.

The properties of the best SiO_2-Al_2O_3-BeO glass, X-2124, and the best modified compositions, X-2285, are compared with the properties of AF-994 and M-glass (YM-31A) in Table IV.

TABLE IV

PROPERTY COMPARISONS

Glass	T.S. $\times 10^3$ psi	E $\times 10^6$ psi	Density, g/cc	Specific Modulus
AF-994	700	12.4	2.49 (fiber)	4.98
YM-31A	500	16.4	2.89 (fiber)	5.67
X-2124	681	14.1	2.41 (bulk)	5.85
X-2285	715	14.95	2.50 (bulk)	5.98

In order to obtain additional data on the properties of X-2124,

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this glass was fiberized in a standard 52-hole laboratory bushing. AF-994 glass fibers were also produced from the same bushing in order to compare the properties of the two glasses when prepared under the same conditions.

X-2124 batch, prepared in the usual manner, was melted in platinum crucibles for 24 hours at 2900°F. The cullet produced from this operation was then fed into the 52-hole bushing. Forming temperatures of 2900°F to 2950°F were utilized to fiberize the glass. In this manner, approximately twenty-five (25) 1/4 lb. packages of forming strand were prepared. Owens-Corning size, P682, was applied to the glass strand during the forming operation.

Standard AF-994 batch was melted in platinum crucibles for 24 hours at 2900°F. The cullet produced from this operation was then fed into the 52-hole bushing. Forming temperatures of 2800°F to 2850°F were utilized to fiberize the glass. In this manner, approximately twenty-five (25) 1/4 lb. packages of forming strand were prepared. Owens-Corning size, P682, was applied to the glass strand during the forming operation.

No major problems were encountered in the forming operation. The glass fiberized well. Proper manipulation of forming temperature, glass head, and pulling speed resulted in an excellent operation. The only problems foreseen in a scale-up of the operation to a full-size 204-hole production unit involved the establishment of the proper process conditions so that the optimum properties are obtained in the glass fibers. As seen from the data below, neither the AF-994 glass nor the X-2124 glass fiberized in the 52-hole bushing had the virgin fiber properties that have been consistently achieved in a one-hole bushing for the X-2124 glass and in commercial production for the AF-994 glass.

Glass	Tensile Strength (psi)	Young's Modulus (psi)
AF-994	478,000	12.2×10^{6}
X-2124	443,0C0	12.1×10^{6}

Using the 1/4 lb. packages of 52-filament strand of both AF-994 and X-2124, the equivalent of single-end roving (204-filaments) was produced by the conventional roving process. Minor adjustments were necessary in taking the strand off the forming package because of its fewer number of filaments and non-standard package build.

Five single-end roving packages were used as the input material to filament wind flat laminates approximately 12" x 6" x 1/8". The resin system used was Epon 828, 10 phr phenyl glycidyl ether,

14 phr metaphenylenediamine (C1). Test specimens parallel to the fibers were cut from these laminates to determine comparative composite properties. Federal Test Method 406 was used in each instance:

Tensile Strength and Modulus	Method 1011
Compressive Strength	Method 1021
Flexural Strength	Method 1031

In the case of the tensile specimens, the test area was reduced to 1/4" width so as to minimize gripping problems. In the case of the flexural specimens, the length was reduced to 3-1/2" (from 4") to maximize the number of specimens attainable from each laminate.

The physical properties of each laminate are as follows:

	AF-994	X-2124
Resin Content	18.0%	33.4%
Specific Gravity	2.03	1.72
Barcol Hardness	75	67
Thickness	.123"	.124"

The mechanical properties of each laminate are given in Table V. For purposes of data comparison, the properties of the AF-994 laminate have been reduced by the law of mixtures to calculated values for a resin content of 50.5% by volume equal to that of the X-2124 laminate.

The data of Table V indicates that at equal glass content, the X-2124 glass gives greater laminate strength and modulus than the AF-994 glass. In view of the fact that these data are not consistent with the virgin filament strengths reported above and are the result of a very limited number of tests, it is recommended that these data not be considered conclusive with respect to the comparative properties of AF-994 and X-2124 glass. A more extensive testing program should be undertaken to conclusively compare these two glasses. This is of major significance in view of the fact that AF-994 glass produced by a standard commercial process has a virgin filament strength of 665,000 psi and a modulus of 12.4×10^6 psi and would give laminates of greater stiffness and strength than reported in Table V.

Several conclusions have been drawn from this study of glass compositions in the SiO_2-Al_2O_3-BeO system.

1. Glasses with the best properties are located at SiO_2 levels of 65 to 70 mole percent with Al_2O_3 to BeO mole ratios of approximately 0.71.

2. Properties of glasses in this region can be improved to

TABLE V

LAMINATE PROPERTIES FOR X-2124 AND AF-994 GLASSES
(NORMALIZED AT A RESIN CONTENT OF 50.5% BY VOLUME)

Property	X-2124 Glass	AF-994 Glass
Tensile Strength (psi)	188,000 (5)	159,000 (3)
Tensile Modulus (psi $\times$ 10^{-6})	6.66 (3)	5.82 (2)
Compressive Strength (psi)	50,200 (3)	40,300 (4)
Compressive Modulus (psi $\times$ 10^{-6})	6.72 (3)	6.29 (2)
Flexural Strength (psi)	180,000 (5)	116,000 (5)
Flexural Modulus (psi $\times$10^{-6})	5.70 (5)	5.92 (5)

() Refers to number of specimens tested

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some extent by the proper addition of a fourth oxide, the best being MgO. This will result, however, in a density increase.

3. In general, glasses based on the SiO_2-Al_2O_3-BeO system must be melted from batch at approximately 2900°F for 24 hours to obtain optimum strength and modulus properties.

c. SiO_2-Al_2O_3-MgO System

This system has continually been of importance because of its potential properties, as shown most notably by AF-994. Work on the system during the previous year has been characterized by the study of properties as influenced by oxide additions, by major changes in the SiO_2 content coupled with large variations in Al_2O_3 to MgO mole ratios, and by changes in melting and forming conditions.

The list of compositions studied and their properties are shown in Table VI. Figure 6 is a portion of the diagram of the SiO_2-Al_2O_3-MgO system showing the location of all three-component glasses studied in the system.

Initial studies dealt with the addition of various oxides to one or more SiO_2-Al_2O_3-MgO glasses for the purpose of studying property variations. Based on the results obtained with X-1857, a glass containing small amounts of ZrO_2, X-2118, X-2119, and X-2120 were melted and fiberized. X-2118 itself was further modified with CaO, TiO_2, and/or Li_2O to yield X-2121, X-2122, and X-2123.

Based on the modulus of X-1857, further ZrO_2 additions had little or no effect on modulus of elasticity. It appears, however, that in some cases qui a large effect is exerted on tensile strength (see X-2118 and X-2119). ZrO_2 does increase overall bulk density when used in a glass as shown by the density of X-2119.

As for the additional use of CaO, Li_2O, and/or TiO_2 in any of these glasses, no beneficial effects would be expected. This is based on the results shown for X-2121, X-2122, and X-2123. Tensile strengths are definitely lowered and moduli are not beneficially affected.

X-2152 through X-2166 represent modifications of the general compositional area in the SiO_2-Al_2O_3-MgO system previously found to have maximum tensile strength and modulus properties, densities less than 2.5 g/cc, and the best fiberization properties. Li_2O in particular has been utilized to check its effect on properties, especially density. X-2152 through X-2155 represent a series of such compositions with decreasing mole percentages of SiO_2. At the same time, the MgO to Li_2O content

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TABLE VI

SiO$_2$ - Al$_2$O$_3$ - MgO System and Modifications

Glass No.		SiO$_2$	Al$_2$O$_3$	MgO	CaO	LiO$_2$	ZrO$_2$	Average Tensile Strength x10^3 psi	Modulus of Elasticity x10^6 psi	Average Diameter x10^{-5} in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
		Oxides (a. weight %, b. mole %)											
X-1857	a.	62.0	25.9	10.0			3.0	511	13.5	31	2770	17	-
	b.	66.6	15.8	16.0			1.5						
X-2118	a.	60.0	25.0	10.0			5.0	745	13.2	19	2795	16	-
	b.	65.2	16.0	16.2			2.6						
X-2119	a.	58.0	25.0	10.0			7.0	777	13.0	20	2795	15	2.62
	b.	63.7	16.2	16.4			3.7						
X-2120	a.	57.0	30.0	10.0			3.0	616	13.1	22	2850	15	-
	b.	62.6	19.4	16.4			1.6						
X-2121	a.	60.0	15.0	10.0	10.0		5.0	436	12.8	40	2680	18	-
	b.	61.9	9.1	15.4	11.1		2.5						
X-2122*	a.	58.0	24.1	9.6	4.0		4.7	475	12.1	47	2735	16	-
	b.	63.3	15.5	15.7	4.5		2.5						
X-2123	a.	56.3	23.4	9.4	4.0	2.1	4.9	426	13.0	35	2620	15	-
	b.	59.3	14.5	14.7	4.5	4.5	2.5						
X-2152	a.	68.4	24.9	4.9		1.8		712	12.8	-	-	-	2.41
	b.	72.7	15.6	7.8		3.9							
X-2	a.	66.9	24.3	6.4		2.4		671	13.0	35	2850	15	2.47
	b.	70.0	15.0	10.0		5.0							

*Balance is TiO$_2$

TABLE VI (Continued)

Glass No.	SiO$_2$	Al$_2$O$_3$	MgO	Li$_2$O	ZrO$_2$	Ta$_2$O$_5$	Average Tensile Strength x10^3 psi	Modulus of Elasticity x10^6 psi	Average Diameter x10^{-5} in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2154	67.5 70.0	24.5 15.0	4.8 5.0	3.2 10.0			671	13.0	27.0	2850	15	2.47
X-2155	61.7 65.0	28.2 17.5	7.4 11.7	2.7 5.8			687	13.0	30.0	2900	15	2.54
X-2156	65.3 69.0	24.1 15.0	6.5 10.0	2.3 5.0	1.9 1.0		678	12.5	37.0	2850	15	2.5
X-2157	64.3 68.3	23.3 14.6	3.2 4.9	4.6 9.8	4.6 2.4		645	11.9	27.0	2850	15	2.49
X-2158	61.4 66.7	22.3 14.3	3.0 4.8	4.3 9.5	9.0 4.8		430	11.2	33.0	2915	15	2.49
X-2159	61.3 66.0	29.8 18.9	2.9 4.7	4.3 9.4	1.7 0.9		660	11.8	30.0	2915	15	2.46
X-2160	57.0 63.0	34.6 22.5	2.7 4.5	4.0 9.0	1.7 0.9		677	11.6	24.0	2915	15	2.5
X-2161	65.8 69.0	24.3 15.0	3.2 5.0	4.7 10.0	2.0 1.0		741	11.7	22.0	2850	15	2.44
X-2162	65.9 69.0	24.3 15.0	2.6 4.0	5.2 11.0	2.0 1.0		710	11.5	23.0	2915	15	2.48
X-2163	66.? 69.0	24.4 15.0	1.9 3.0	5.7 12.0	2.0 1.0		671	11.0	28.0	2915	14	2.39

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TABLE VI (Continued)

Glass No.	SiO2	Al2O3	MgO	Li2O	ZrO2	Ta2O5	Average Tensile Strength x 10³ psi	Modulus of Elasticity x 10⁶ psi	Average Diameter x 10⁻⁵ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2164	60.1 / 64.0	27.9 / 17.5	7.4 / 11.7	2.7 / 5.8	1.9 / 1.0		530	11.8	36.0	2800	15	2.5
X-2165	65.6 / 69.0	24.2 / 15.0	4.5 / 7.0	3.8 / 8.0	1.9 / 1.0		720	11.5	23.0	2795	14	2.51
X-2166	65.0 / 69.5	23.8 / 15.0	3.2 / 5.0	4.6 / 10.0		3.4 / 0.5	688	11.5	26.0	2850	15	2.45
X-2262	60.0 / 68.1	35.0 / 23.4	5.0 / 8.5				561	12.5	48	3190	15	2.5
X-2263	55.0 / 60.8	35.0 / 22.8	10.0 / 16.5				644	13.6	35	2955	15	2.6
X-2264	55.0 / 57.9	30.0 / 18.6	15.0 / 23.5				704	12.9	22	2735	18	2.6
X-2265	55.0 / 55.2	25.0 / 14.8	20.0 / 30.0				389	-	39	2575	15	2.6
X-2266	65.0 / 62.7	15.0 / 8.5	20.0 / 28.8				486	11.8	31	2735	16	2.6
X-2267	51.3 / 55.5	34.9 / 22.2	13.8 / 22.3				578	13.1	40	2760	15	2.6
X-2268	50.0 / 56.5	40.0 / 26.6	10.0 / 16.9				Could not be fiberized					

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TABLE VI (Continued)

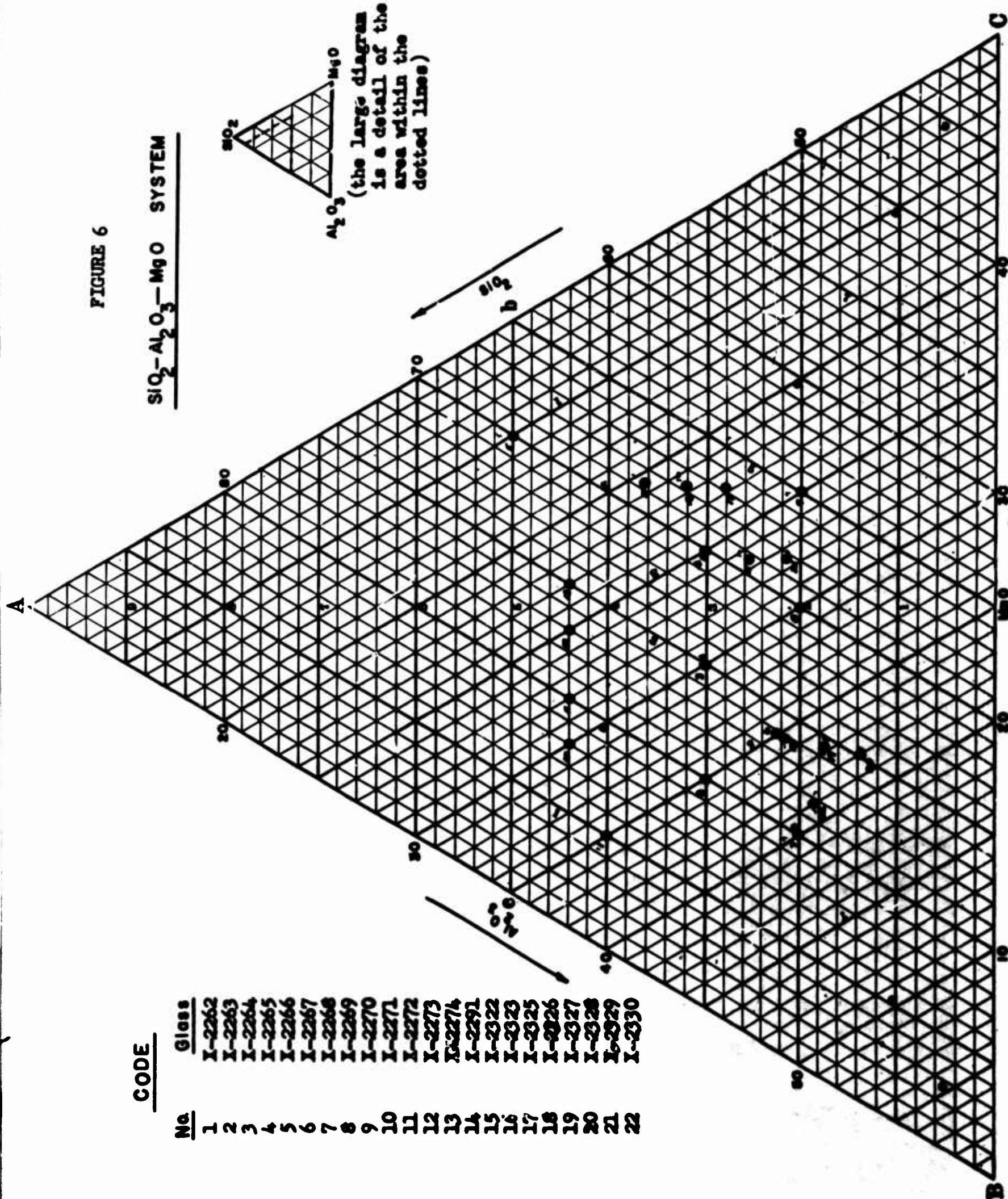| Glass No.	SiO₂	Al₂O₃	MgO	Li₂O	ZrO₂	Ta₂O₅	Average Tensile Strength x 10³ psi	Modulus of Elasticity x 10⁶ psi	Average Diameter x 10⁻⁵ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2269	50.0	30.0	20.0				497	13.4	48	2560	13	2.7
	51.3	18.1	30.6									
X-2270	50.0	25.0	25.0				377	13.3	51	2445	15	2.7
	49.0	14.4	36.6									
X-2271	62.0	30.0	8.0				603	13.5	46	2915	15	2.6
	67.7	19.3	13.0									
X-2272	62.0	28.0	10.0				845	12.2	17	2850	15	2.5
	66.4	17.7	16.0									
X-2273	62.0	25.0	13.0				703	11.9	19	2750	15	2.5
	64.5	15.3	20.2									
X-2274	62.0	23.0	15.0				727	12.0	22	2700	15	2.6
	63.3	13.8	22.8									
X-2291	58.06	20.74	21.19				729	13.1	23	3600	17	2.6
	56.99	11.99	31.02									
X-2322	52.68	26.43	20.88				543	13.4	40	2600	15	2.6
	53.00	15.67	31.33									
X-2323	56.1	21.7	22.2				660	13.4	35	2515	15	2.68
	55.0	12.5	32.5									
X-2325	54.05	22.83	23.12				466	13.2	38	2450	15	2.64
	53.00	13.19	33.81									

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TABLE VI (Continued)

Glass No.	SiO₂	Al₂O₃	MgO	Li₂O	ZrO₂	Ta₂O₅	Average Tensile Strength x10³ psi	Modulus of Elasticity x10⁶ psi	Average Diameter x10⁻⁵ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2326	50.8 / 55.0	35.3 / 22.5	13.9 / 22.5				614	13.6	39	2750	15	2.6
X-2327	48.8 / 53.0	36.7 / 23.5	14.5 / 23.5				698	13.5	27	2740	15	2.65
X-2328	46.8 / 51.0	38.1 / 24.5	15.1 / 24.5				569	13.6	48	2835	15	2.67
X-2329	50.7 / 51.0	27.5 / 16.33	21.8 / 32.67				671	14.0	30	2670	15	2.63
X-2330	49.3 / 55.0	39.0 / 25.6	11.7 / 19.4				432	13.5	61	3015	5	2.68

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TABLE VI (Continued)

Glass No.	SiO_2	Al_2O_3	MgO	Li_2O	ZrO_2	Ta_2O_5	Average Tensile Strength $\times 10^3$ psi	Modulus of Elasticity $\times 10^6$ psi	Average Diameter $\times 10^{-5}$ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2326	50.8 / 55.0	35.3 / 22.5	13.9 / 22.5				614	13.6	39	2750	15	2.6
X-2327	48.8 / 53.0	36.7 / 23.5	14.5 / 23.5				698	13.5	27	2740	15	2.65
X-2328	46.8 / 51.0	38.1 / 24.5	15.1 / 24.5				569	13.6	48	2835	15	2.67
X-2329	50.7 / 51.0	27.5 / 16.33	21.8 / 32.67				671	14.0	30	2670	15	2.63
X-2330	49.3 / 55.0	39.0 / 25.6	11.7 / 19.4				432	13.5	61	3015	5	2.68

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FIGURE 6

$SiO_2 - Al_2O_3 - MgO$ SYSTEM

(the large diagram is a detail of the area within the dotted lines)

CODE

No.	Glass
1	L-2262
2	L-2263
3	L-2264
4	L-2265
5	L-2266
6	L-2267
7	L-2268
8	L-2269
9	L-2270
10	L-2271
11	L-2272
12	L-2273
13	L-2274
14	L-2291
15	L-2322
16	L-2323
17	L-2325
18	L-2326
19	L-2327
20	L-2328
21	L-2329
22	L-2330

has been varied. As shown by the data, small amounts of Li_2O can produce densities as low as 2.41 g/cc. In this series of four glasses, a reduction in the SiO_2 content causes an increase in the density and the modulus of elasticity. Therefore, the desirable qualties of both low density and high modulus cannot be obtained in this series of compositions. Nevertheless, glasses represented by X-2152, X-2154, and X-2155 are obtainable with specific moduli which are greater than that of AF-994.

X-2156 through X-2165 represent compositions containing ZrO_2 in addition to Li_2O. Again, ZrO_2 was added because of its reported effect on modulus. X-2166 contains Ta_2O_5 for the same reason. The results indicate, however, that neither addition improves the modulus. In fact, in all cases the modulus values are lower than those found for X-2152 through X-2155. The tensile strength figures for this series, for the most part, are relatively good, especially in the case of X-2161, X-2162 and X-2165.

It is concluded that several oxide additions can be made to the basic SiO_2-Al_2O_3-MgO system to obtain one specific result. However, attempts to lower density while improving modulus and tensile strength are unlikely to meet with success.

The glasses designated X-2262 through X-2270 were selected from compositional areas normally not associated with optimum forming characteristics. It was felt that studies of such areas might reveal improved fiber properties which had previously been overlooked. Note that most of the compositions contain less than 60 mole percent SiO_2. Those above 60 mole percent SiO_2 have Al_2O_3 to MgO mole ratios well below or well above 1.0. None of the glasses have noteworthy properties. Though one or two may have good strength or modulus properties, all have high densities. This is very evident for those glasses with less than 56 mole percent SiO_2. Such densities, of course, reduce the final specific strength and specific modulus of the glasses in question.

Glasses designated X-2271 through X-2274 show the influence of an increase in the SiO_2 content. The strength has improved and the density has begun to drop.

The remaining compositions fiberized in the SiO_2-Al_2O_3-MgO system are shown in Table VI (X-2322 through X-2330). These were based on the results of work performed under the section of this report titled "Relationship Between Composition and Properties of Selected Glasses." Data for the SiO_2-Al_2O_3-MgO system is summarized in Figure 7, Modulus vs. 2Al/MgO, which indicates that modulus increases as the SiO_2 content decreases and, is a maximum at either very high or very low Al_2O_3 to MgO mole ratios.

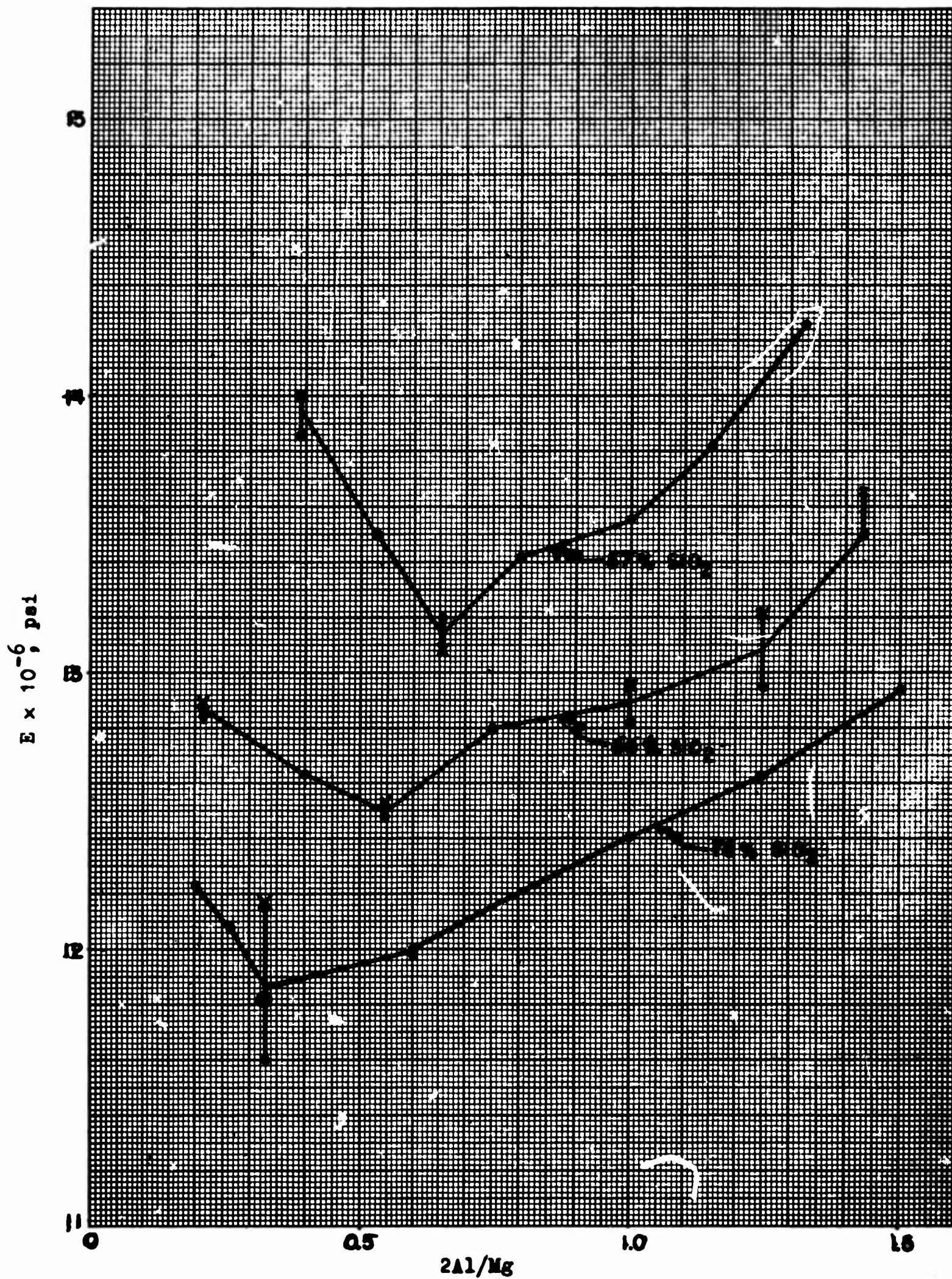Figure 7 was used, therefore, to design glasses having high

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Figure 7 Modulus vs. 2Al/Mg Ratio

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moduli of elasticity. In general, as demonstrated previously, decreases in SiO_2 content improved modulus at a given Al_2O_3 to MgO mole ratio. In general, this also produced an increase in density. The relatively high tensile strengths of the series represented by X-2322 through X-2330 were obtained through careful melting history changes and fiberization techniques. At such low SiO_2 contents the glass viscosity was relatively low, which necessitated fiberization in bushings with small tips (0.040" to 0.050"). Normal fiberization techniques would have produced rather low strength fibers and in some cases the glasses could not have been fiberized at all. In conclusion, it appears that thermal history and fiberization technique is quite important with glasses of this nature.

A study of the tensile strength and modulus of AF-994 glass as affected by thermal history and fiberization technique (forming temperature, forming time, and orifice size) was made to complete the investigation of the SiO_2-Al_2O_3-MgO system. It was felt that a study of this nature, taken in the context of the overall investigation, would aid in selecting optimum forming conditions for most of the glasses based on SiO_2, Al_2O_3, and MgO or R_xO substitutions for MgO.

The program was carried out as follows:

1. AF-994, melted from batch at 2900°F for four hours, was fiberized in one of three one-hole bushings having hole sizes of 0.062", 0.050" and 0.040" respectively.

2. The glass was fiberized at temperatures as low as possible and temperature was increased in increments of 25° to a maximum of 3000°F.

3. The glass was fiberized for a period of eight hours at each temperature and fiber samples for tensile strength measurements were taken hourly.

4. Fiber samples for modulus of elasticity measurements were taken every two hours at each forming temperature over the eight-hour period.

5. The average fiber diameter for all samples was held between 0.00025" and 0.00035". Glass level was held relatively constant at 1.5" to 2.0".

The results obtained in this study are shown in Table VII. Both the tensile strength and modulus figures shown are the maximum values obtained over the eight-hour period. The sub-number in parenthesis is the number of hours the glass was fiberized at the given forming temperature before its maximum strength was obtained.

The tensile strength values show a dependence on the length of time the glass has been in the bushing. Most of the runs reached

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TABLE VII

Effect of Forming Temperature and Orifice Size on AF-994 Tensile Strength and Modulus of Elasticity

Forming Temp. °F	2725	2750	2775	2800	2825	2850	2875	2900	2925	2950	2975	3000
Orifice Size = 0.040"												
T.S. x 10³ psi	-	-	-	811(6)*	785(7)	660(3)	757(3)	654(2)	779(3)	700(4)	728(7)	740(
E x 10⁶ psi	-	-	-	12.4	13.7	13.2	13.3	13.1	13.5	13.2	12.8	12.6
Orifice Size = 0.050"												
T.S. x 10³ psi	-	756(6)	800(6)	791(2)	780(3)	801(7)	809(6)	790(2)	768(6)	769(7)	732(4)	704(
E x 10⁶ psi	-	12.9	13.8	13.3	13.3	13.3	13.1	13.7	13.5	13.0	12.7	12.7
Orifice Size = 0.062"												
T.S. x 10³ psi	721 (4)	734(8)	768(6)	750(7)	753(8)	791(5)	786(7)	781(8)	763(2)	790(7)	760(3)	740(
E x 10⁶ psi	12.7	13.4	13.0	13.1	12.7	12.7	12.9	12.9	13.0	13.7	-	13.1

*No. of hours required to reach given strength

maximum tensile strength values in four to seven hours. It should also be noted that the highest strengths are not obtained until the forming temperature has reached 2775°F or higher. Apparently, forming temperatures above 2900°F do not produce increasingly higher tensile strengths.

There is some indication that the orifice size influences strength to a small extent. This might be a thermal history effect caused by a different quench rate for the smaller orifice. Once the forming temperature reaches 2850°F, however, there is no noticeable difference in strength.(These statements apply to comparisons between fibers from the 0.050" and 0.062" orifice. Fiber strengths from the 0.040" orifice are rather variable and were probably adversely influenced by interactions of the fiber cone and the edge of the small orifice).

The modulus does not appear to be materially affected by forming temperature, forming time or orifice diameter.

Several conclusions have been drawn from this rather extensive study of glass compositions in the SiO_2-Al_2O_3-MgO system.

1. Glasses with the best combination of tensile strength, modulus of elasticity, density, and forming characteristics are located at an approximate Al_2O_3 to MgO mole ratio of 1.0 and at a SiO_2 level ranging from 60 to 70% by weight.

2. The modulus of elasticity of these glasses can be increased by lowering the SiO_2 content. However, this will also cause an increase in the glass density. The density can be controlled to some extent by using small amounts of Li_2O.

3. Small ZrO_2 additions increase tensile strength under certain conditions, but glass density increases.

4. Compositions with less than 56 mole percent SiO_2 have densities greatly in excess of 2.6 g/cc.

5. If low density is not desired, glasses can be fiberized with moduli of $13 - 14 \times 10^6$ psi and strengths approaching 700,000 psi.

d. SiO_2-Al_2O_3-Li_2O System

The SiO_2-Al_2O_3-Li_2O system was investigated rather extensively under the first year's effort and these results were reported in Technical Report AFML-TR-65-90, Part I. However, in order to investigate compositions outside optimum fiberization areas, eight additional glasses were subsequently prepared.

The compositions (X-2172, X-2245 through X-2251) and their properties are shown in Table VIII under the heading "SiO_2-Al_2O_3-Li_2O System." The position of each composition is plotted on the three-phase diagram, Figure 8.
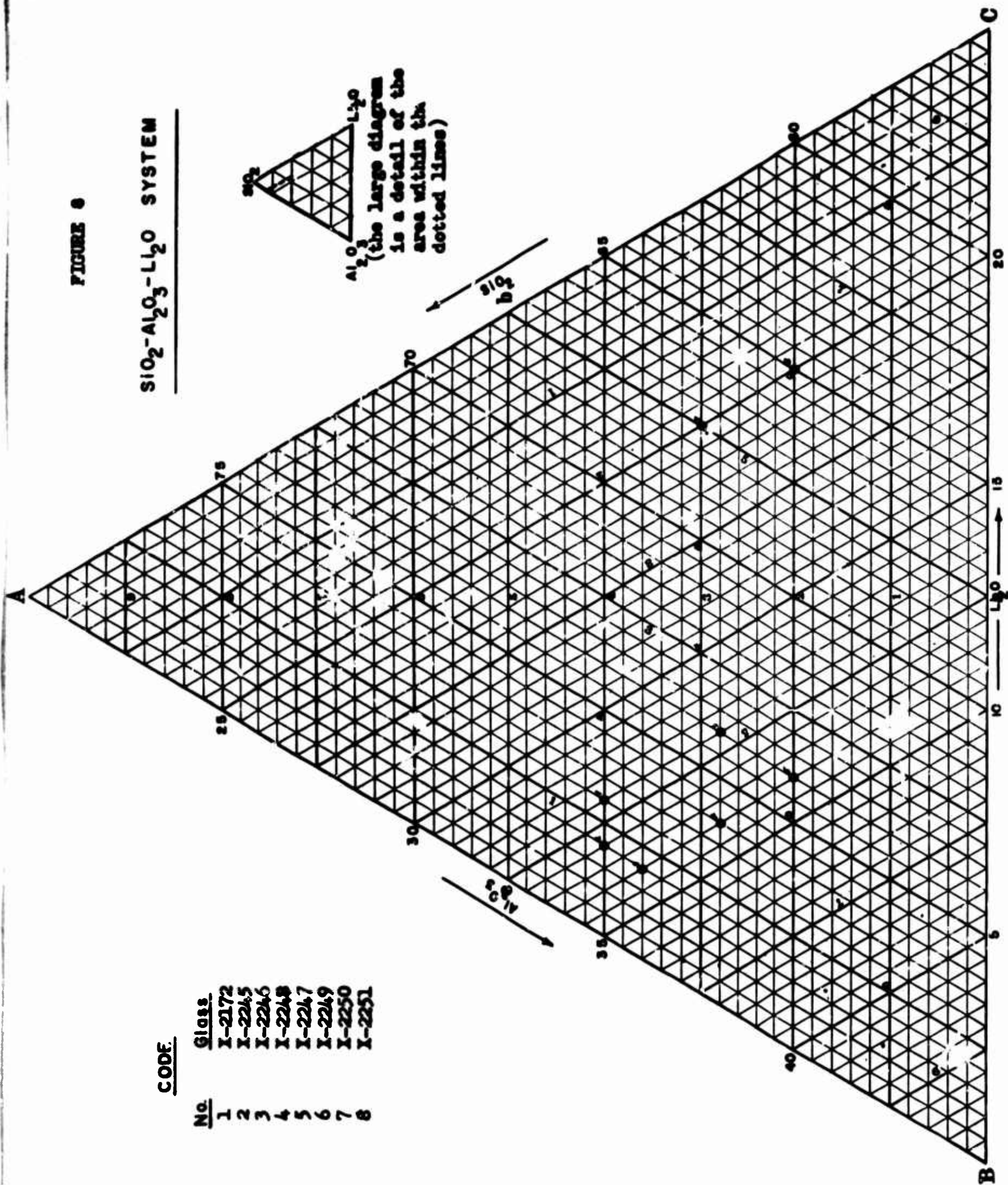
TABLE VIII

SiO_2 - Al_2O_3 - Li_2O System

Glass No.		Oxides (a. weight %, b. mole %) SiO_2	Al_2O_3	Li_2O	Average Tensile Strength $\times 10^3$ psi	Modulus of Elasticity $\times 10^6$ psi	Average Diameter $\times 10^{-5}$ in.	Forming Temp. °F	No. of Fibers	Bulk Density g/cc
X-2172	a. b.	65.0 72.3	32.0 21.0	3.0 6.7	698	11.4	31	3115	16	2.4
X-2245		65.0 73.5	33.0 22.0	2.0 4.6	455	10.6	32	3215	15	2.3
X-2246		64.0 72.7	34.0 22.7	2.0 4.6	372	11.8	67	3190	15	2.45
X-2247		60.0 65.1	34.0 21.7	6.0 13.1	522	11.2	26	2800	15	2.4
X-2248		62.0 68.8	34.0 22.2	4.0 9.0	655	11.1	37	3065	18	2.3
X-2249		62.0 66.7	32.0 20.3	6.0 13.0	575	10.7	17	2830	15	2.4
X-2250		62.5 61.0	25.0 14.4	12.5 24.6	306	9.6	22	2390	15	2.4
X-2251		60.0 57.2	25.0 14.0	15.0 28.8	315	10.1	33	2285	15	2.4

FIGURE 8

SiO₂-Al₂O₃-Li₂O SYSTEM

CODE:

No.	Glass
1	X-2172
2	X-2245
3	X-2246
4	X-2248
5	X-2247
6	X-2249
7	X-2250
8	X-2251

The bulk densities of these ⊥ sses were low, as expected.

Several had tensile strengths approaching 700,000 psi.
Modulus values did not exceed 12×10^6 psi. The higher
strength glasses did not correspond with the higher modulus
glasses.

All efforts with the SiO_2-Al_2O_3-Li_2O glasses continued to
indicate that glasses with the best properties in the system
contain approximately 65% by weight SiO_2 and 3 to 5 weight
percent Li_2O. All other compositions investigated failed to
produce better properties, no matter what the fiberization
parameters. The system is capable of producing low density
glasses with good tensile strength properties ($\approx$ 700,000 psi),
but only moderate modulus of elasticity properties
(11- 12×10^6 psi).

e. High Modulus Glasses

A series of compositions were prepared strictly on the basis of
their high modulus properties. Low density and high strength
were not initially considered. Lowenstein's(2) study of high
modulus compositions was used as a guide. BeO was used in
only one case to determine its effect on final properties.

The compositions studied and their properties are shown in
Table IX titled "Compositions Prepared For High Modulus Studies."

As suggested by Lowenstein, initial studies of possible high
modulus glasses started with those having a low content of
network formers and a high content of network modifying ions.
X-2066 through X-2069 were glasses of this type. X-2067 was
found to have the best fiberization properties in the series.
Various modifications of X-2067 were then made, an increase
in the Al_2O_3 content being most beneficial in increasing the
modulus, as shown by X-2070. X-2073 and X-2117 represent higher and
higher Al_2O_3 contents with corresponding increases in the modulus.
This characteristic of Al_2O_3 was unexpected since it is class-
ified as a network former, in conjunction with SiO_2, in
Lowenstein's study. There also appeared to be some improvement
in tensile strength with the increase in Al_2O_3 content.

At this point X-2117 had the best modulus. X-2130 and X-2131
represent modifications of X-2117 and contain more Al_2O_3 and
changes in the MgO to CaO mole ratio. X-2131 possessed a good
modulus and, unexpectedly, a high tensile strength.

The remaining glasses are modifications of X-2131. The modifi-
cations consist primarily of changes in the MgO to CaO mole
ratio. X-2134 had the best modulus of all glasses studied and,
again unexpectedly, a good tensile strength.

It appears that the best range of components for this particular

TABLE IX

Compositions Prepared For High Modulus Studies

Glass No.		Oxides (a. weight %, b. mole %)									Modulus of Elasticity x10^6 psi	Average Tensile Strength x10^3 psi	Forming Temp. °F	Bulk Density g/cc
		SiO_2	Al_2O_3	CaO	MgO	TiO_2	ZrO_2	CeO_2	Li_2O	BeO				
X-2066	a.	47.9	10.6	10.6	10.6	16.0	4.3	6.0			13.1	335	2365	-
	b.	50.2	6.5	11.9	16.6	12.6	2.2	2.3						
X-2067		45.0	10.0	10.0	10.0	15.0	4.0	6.0			13.3	385	2285	-
		49.0	6.4	11.7	16.2	12.3	2.1	2.3						
X-2068		50.0	10.0	5.0	10.0	15.0	4.0	6.0			13.6	255	2390	-
		54.7	6.4	5.9	16.3	12.3	2.1	2.3						
X-2069		45.0	10.0	5.0	10.0	16.0	4.0	10.0			12.6	324	2325	-
		50.8	6.6	6.0	16.8	13.6	2.2	3.9						
X-2070		42.9	14.3	9.5	9.5	14.3	3.8	5.7			14.2	522	2310	-
		47.5	9.3	11.3	15.7	11.9	2.1	2.2						
X-2071		52.7	22.7		9.1	9.1	6.4				13.4	328	2735	-
		58.8	14.9		15.1	7.6	3.5							
X-2072		54.6	22.7		9.1	9.1	4.6				13.1	455	2735	-
		60.2	14.8		15.0	7.6	2.4							
X-2073		40.9	18.2	9.1	9.1	13.6	3.6	5.5			14.5	462	2315	-
		46.0	12.1	11.0	15.3	11.5	2.0	2.1						
X-2074		43.1	14.3	10.0	7.6	7.2	3.9	10.6	2.7		14.0	360	2180	-
		47.5	9.3	12.5	12.5	6.0	2.1	4.1	6.0					
X-2117		38.6	23.0	8.6	8.6	12.9	3.4	5.3			14.6	413	2340	-
		44.2	15.5	10.6	14.7	11.1	1.9	2.0						

Table IX (Continued)

Glass No.	SiO$_2$	Al$_2$O$_3$	CaO	MgO	TiO$_2$	ZrO$_2$	CeO$_2$	Li$_2$O	BeO	Modulus of Elasticity x10^6 psi	Average Tensile Strength x10^3 psi	Forming Temp. °F	Bulk Density g/cc
X-2130	38.3 / 45.0	28.9 / 20.0	4.0 / 5.0	6.8 / 12.0	12.4 / 11.0	3.5 / 2.0	4.9 / 2.0	1.3 / 3.0		14.3	305	2390	-
X-2131	38.2 / 45.0	28.8 / 20.0	7.1 / 9.0	7.4 / 13.0	10.2 / 9.0	3.5 / 2.0	4.9 / 2.0			14.5-15.3	733	2505	2.91
X-2133	38.3 / 45.0	28.9 / 20.0	5.8 / 7.3	8.4 / 14.7	10.0 / 9.0	3.5 / 2.0	4.9 / 2.0			Couldn't Obtain	393	2340	2.86
X-2134	37.7 / 45.0	28.4 / 20.0	11.5 / 14.7	4.1 / 7.3	10.0 / 9.0	3.4 / 2.0	4.8 / 2.0			15.7	656	2535	3.4
X-2135	43.7 / 50.0	22.3 / 15.0	7.3 / 9.0	7.6 / 13.0	10.5 / 9.0	3.6 / 2.0	5.0 / 2.0			15.0	655	2505	2.9
X-2136	38.0 / 45.0	28.7 / 20.0	8.7 / 11.0	6.2 / 11.0	10.1 / 9.0	3.5 / 2.0	4.8 / 2.0			14.7	456	2410	3.0
X-2137	39.8 / 47.0	25.9 / 18.0	11.6 / 14.7	4.2 / 7.3	10.1 / 9.0	3.5 / 2.0	4.9 / 2.0			14.0	519	2505	2.9
X-2169	39.5 / 43.0	28.1 / 18.0	12.6 / 14.7	4.5 / 7.3	8.5 / 7.0	3.8 / 2.0			3.1 / 8.0	Could Not Be Fiberized			

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glass series is:

Oxide	Mole %
SiO_2	45 (approx.)
Al_2O_3	20
CaO/MgO	2/1
TiO_2	10
ZrO_2	2
CeO_2	2

The use of BeO, at least in this series of glasses, is detrimental to the glass as shown by the fiberization problems with X-2169. The bulk densities of all glasses investigated are high, of course, but are not unexpected.

SECTION III

Relationship Between Composition and Properties of Selected Glasses

1. ### Background Relating to Study

Glass fibers with the highest possible tensile strength and modulus of elasticity are desired for many important applications. These properties are intimately related to the ultimate structure of glass. Knowledge of the structure of a glass and its relationship to these properties would be invaluable in developing new glass compositions with superior performance.

The work reported here started as an attempt to find out whether modulus of elasticity and tensile strength of fibers could be related to glass composition and presumably structure in the same manner as has been done with certain other properties. For instance, Day and Rindone (3,4) have shown that a number of physical properties of glasses in the SiO_2-Al_2O_3-Na_2O field vary in a systematic manner with composition changes. Further, composition vs. property curves usually show breaks which they related to a proposed theory of changes in glass structure. In sets of related compositions, breaks occur at the points where the Al to Na ratio is one. It was postulated that at ratios below one, the aluminum is in fourfold coordination and participates in the network, while at higher ratios some of the aluminum assumes sixfold coordination and acts as a modifier. At a ratio of Al to Na of one, there are just enough oxygens present to supply two for each Si and Al ion, the ratio needed for fourfold coordination.

Earlier work on the same project[1] showed that a break at Al to Na ratios of one exists in the SiO_2-Al_2O_3-Na_2O field for the properties of modulus of elasticity, tensile strength, and

fiber forming temperature. These results led to the study reported here in which several other oxides from Group 1 or 2 in the periodic table were substituted for Na_2O.

2. Experimental Procedure

a. Formulation of Compositions Studied

Compositions were calculated on a mole percent basis, and corresponded in general to those selected for the original study in the SiO_2-Al_2O_3-Na_2O field. Batches were formulated at three arbitrarily selected SiO_2 contents, 75, 66, and 57 mole percent. The following oxides were included in the study: K_2O, Li_2O, mixtures of K_2O and Li_2O, MgO, CaO, ZnO and BeO.

Batches were formulated from a high purity commercial potter's flint, commercial calcined alumina of 99.5% purity, and U.S.P. quality K_2CO_3, Li_2CO_3, $CaCo_3$, MgO, ZnO and BeO.

b. Preparation of Melts

Batches were prepared and melted essentially as described previously in Section II. The glasses were crushed and remelted once in each case to improve homogeneity. Melting times and temperatures varied between glasses. A combination of time and temperature was selected which was adequate to produce nearly seed-free glass. Usually melting periods were one hour each, with the temperature adjusted as required. However, longer melting times were used with the most visc glasses. Maximum melting temperatures were around 3150^c. Crucibles used for melting ZnO were covered with lids during the melting process to minimize volatilization of ZnO. A few crucibles with contents were weighed before and after melting the batch. The loss in weight attributable to volatilization was small enough to justify the conclusion that losses of ZnO could be ignored for purposes of the present study.

c. Preparation of Fibers

Fibers for testing were made in a one hole bushing. In general a pulling speed of 6125 feet per minute was used for tensile strength fibers. In the case of some very viscous glasses and several of the lithia glasses, it was necessary to reduce the speed. In the case of the viscous glasses, the speed was reduced to avoid excessive bushing temperatures. Some of the lithia glasses had to be run at lower speeds because the forming cones became unstable at the temperatures required for the desired fiber diameters.

Note was taken of the forming temperature as measured by a thermocouple attached to the bushing wall near the tip. These temperatures gave some indication of relative glass viscos-

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ities, but large variations were introduced because of bushing changes, drift of the thermocouple output with time, and modifications of forming procedure necessary with some of the glasses.

The target fiber diameter for tensile strength measurements was 0.00035 to 0.00040 inches. Some fibers were taken which were outside this range, particularly in the case of glasses that were especially hard to fiberize. However, all tests included fibers in this range, and it is felt that changes in fiber diameter between tests was not an important factor. Fibers were captured and mounted on forks in a manner that permitted the testing of sections of untouched fiber. In this case, each fork contained only five fibers, the maximum amount conveniently obtained in one capture with the bushing position used.

The target fiber diameter for fibers used for measuring modulus was 0.00070 to 0.00080 inches. Modulus fibers were prepared at the same temperature as tensile strength fibers. The increased diameter was obtained by slowing down the winder as required. Usually this speed was about 1000 feet per minute. The above target for fiber diameters was selected because it is a convenient size to handle and because it was noticed earlier that results were influenced somewhat by fiber diameter. Some fibers outside the above limits were used, particularly in the case of glasses that proved especially hard to fiberize. However, since in all cases some fibers were in this range, and all were close to it, it is felt that variation in fiber diameter from the target was not responsible for any serious errors.

d. Tensile Strength Measurement

Fibers were transferred on the forks on which they were collected to the tensile strength tester described in Section II and shown as Figure 1 (Page 3). Usually, fibers were tested within an hour after being prepared. A normal test consist u of three sets of three forks each, with five breaks per fork. In a few cases where fibers were extremely difficult to obtain, only three forks were prepared.

Fiber diameters were determined on fragments of fibers remaining on the forks, since in most cases the sections tested were completely destroyed. Diameters were measured on the microscope by means of an eyepiece with movable crosshair. Fibers to be measured were immersed in an oil of slightly lower index, selected so that the fiber edges appeared reasonably sharp. In some cases, measurements were cross-checked using the Vickers Image-Splitting Eyepiece. The same values were obtained.

e. Modulus of Elasticity Measurement

Modulus of elasticity was measured on sections of fibers

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about 14 inches long by determining the amount of elongation under loads of 5 and 10 grams. Normally measurements were made at these two loadings on five fibers, so that each point reported is the average of ten determinations. The apparatus is pictured in Figure 2 (Page 4).

Fiber diameters were measured optically in the same manner as were those used for tensile strength.

f. **Density Measurement**

In a few cases, glass densities were run. Pieces of cullet about a gram in weight were annealed and run by the Archimedes method, using distilled water as the immersion medium. It is possible that some of the glasses were slightly soluble in water, and that precision could have been improved by selection of a more inert liquid. However, in view of the short time of immersion involved and the precision required, it was felt that results with the distilled water were acceptable.

3. **Results**

a. **SiO_2-Al_2O_3-K_2O System**

Compositions studied and results obtained are given in Table X. In general, glasses in this system were more difficult to fiberize than those in the SiO_2-Al_2O_3-Na_2O system. They were more viscous than the corresponding Na_2O glasses, and devitrified more readily and at higher temperatures. The glass at the 75% SiO_2 level and Al/K ratio of 1.0 could not be fiberized at temperatures attainable because of its high viscosity. The glass at the 57% SiO_2 level and Al/K ratio of 1.0 devitrified too readily to permit fiber forming. All glasses at Al/K ratios higher than 1.0 were too viscous to fiberize at normal pulling speeds. Specimens obtained from them were formed at reduced speeds. Consequently, the temperatures reported in Table X do not represent accurate indications of relative glass viscosities. However, they indicate that there is a break in the viscosity- composition curve at or near the point at which the Al/K ratio is 1.0.

Tensile strength results are consistent with the expectation that there should be a break at an Al/K ratio of 1.0, but are too variable to establish this with certainty. Data could not be obtained for two of the series at the points at which the Al/K ratio is 1.0. Further, results shown for the higher ratios were obtained on fibers pulled at reduced speeds, so that strengths obtained cannot be reliably compared with those pulled at normal speeds.

In Figure 9, modulus is plotted as a function of composition. Part of the curves for the 75% and the 57% SiO_2 levels is

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TABLE X

Compositions and Properties of Silica-Alumina-Potash Glasses

Glass #	X-2001	X-2002	X-2003	X-2004	X-2005	X-2006	X-2007
Composition							
Mole % SiO_2	75.00	75.00	75.00	75.00	75.00	75.00	75.00
Al_2O_3	-	3.13	6.25	9.38	12.50	15.00	16.25
K_2O	25.00	21.88	18.75	15.63	12.50	10.00	8.75
Ave. Tensile Strength x 10^{-3} psi	94	175	235	385	Could not form test fibers		
Ave. Modulus x 10^{-6}, psi	5.44	6.18	7.11	7.85	-	8.83*	9.83
Forming Temp °F	2435	2760	3010	3200	Over 3200	3205*	3205*

Glass #	X-2008	X-2009	X-2010	X-2011	X-2012	X-2013	X-2014
Composition							
Mole % SiO_2	66.00	66.00	66.00	66.00	66.00	66.00	66.00
Al_2O_3	-	6.00	12.00	17.00	20.00	22.00	24.00
K_2O	34.00	28.00	22.00	17.00	14.00	12.00	10.00
Ave. Tensile Strength x 10^{-3} psi	76	162	228	177*	240*	192*	-
Ave. Modulus x 10^{-6} psi	4.45	5.56	7.41	7.55*	8.39*	9.44*	9.94*
Forming Temp °F	2235	2670	3060	3200	3220	3200	3200

Glass #	X-2015	X-2016	X-2017	X-2018	X-2019	X-2020	X-2021	X-2022
Composition								
Mole % SiO_2	57.00	57.00	57.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	-	6.00	12.00	17.00	21.50	24.50	27.50	30.50
K_2O	43.00	37.00	31.00	26.00	21.50	18.50	15.50	12.50
Ave. Tensile Strength x 10^{-3} psi	Too weak to test	134	232	333	Could not run	384	395	Could not run
Ave. Modulus x 10^{-6} psi	Too weak to test	5.00	6.56	8.13	-	9.10	9.63	
Forming Temp °F	-	2505	2975	3205*	Over 3200	3205*	3205*	

*Pulled fibers at speeds lower than normal

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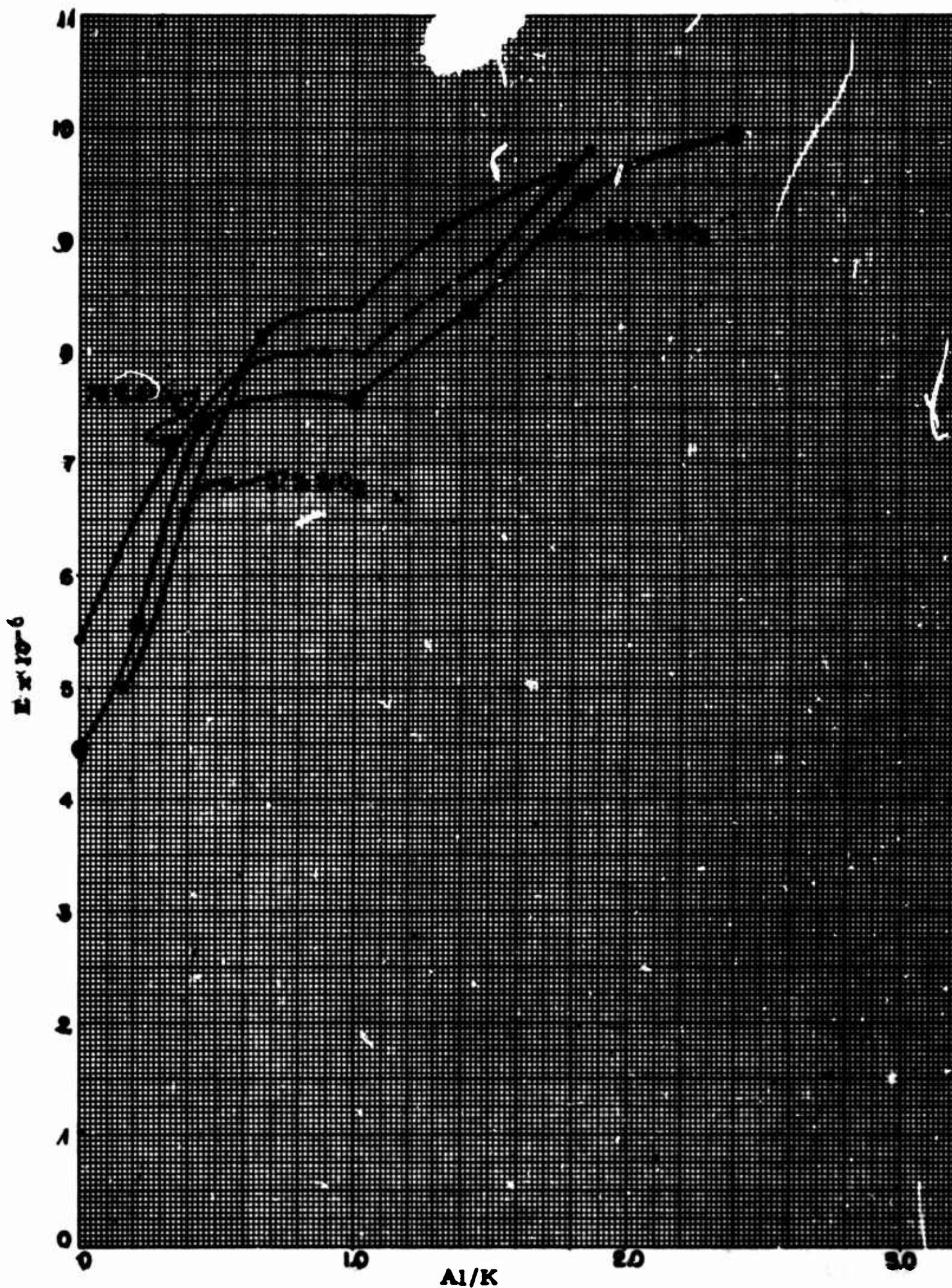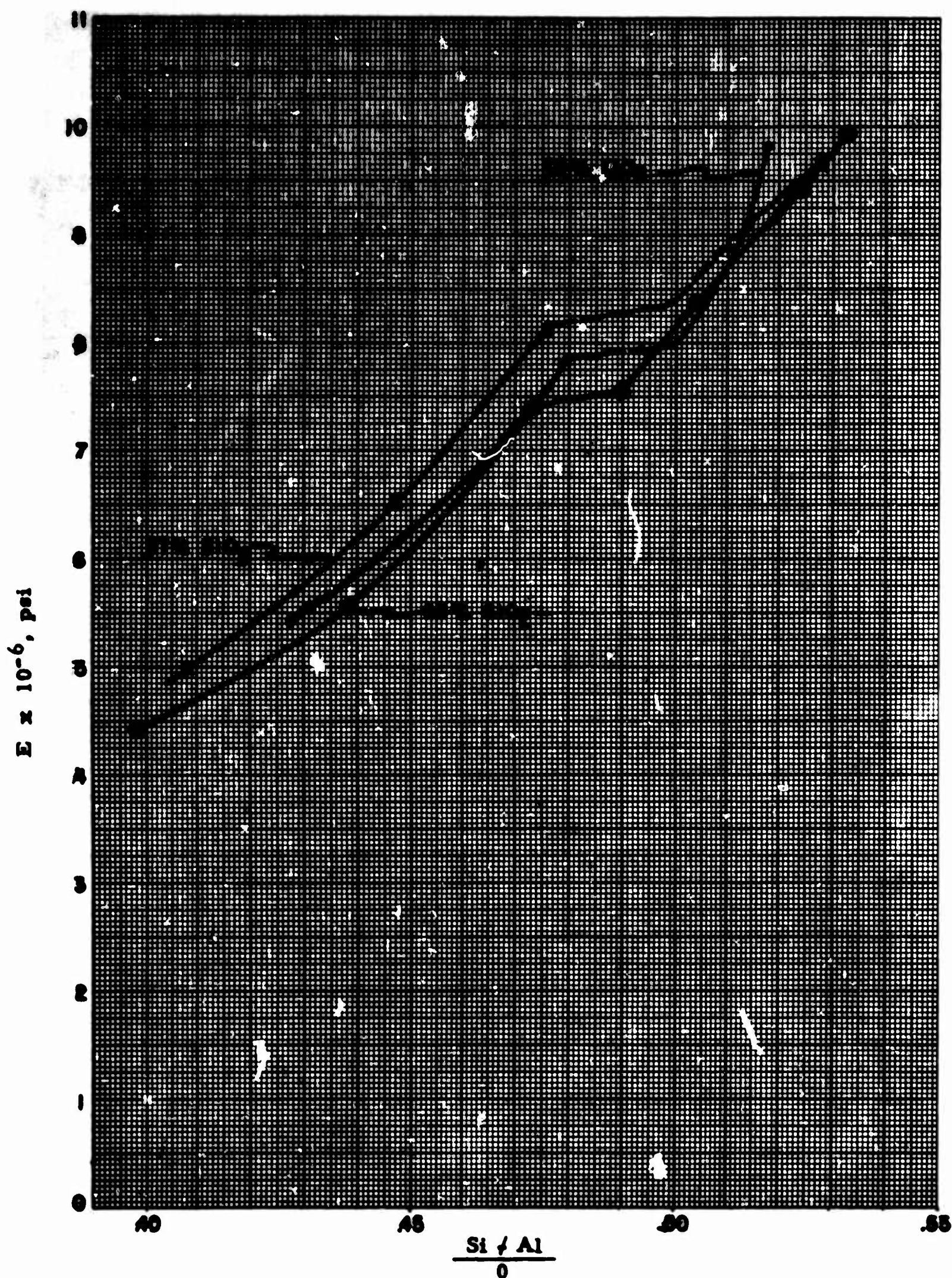Figure 9 Modulus Vs. Al/K Ratio

Figure 10 Modulus vs. $\frac{Si + Al}{0}$ Ratio For Glasses Containing K_2O

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dotted because of missing data. They are drawn to show a break at an Al/K ratio of 1.0. It seems probable that such a break exists from the location of the other points and because of the existence of a break at the 66% SiO_2 level.

Modulus is plotted as a function of the ratio of Si plus Al to O in Figure 10. This relationship was used in studying the SiO_2-Al_2O_3-Na_2O system to indicate that there was some dependence of the properties on the amount of Si present also. In both systems, the curves show two breaks, one at 0.5 (where the Al/K ratio is 1.0) and one at about 0.475. The significance of the latter value has not been determined.

The moduli of the potash glasses are lower than those of the corresponding soda glasses.

b. SiO_2-Al_2O_3-Li_2O System

Compositions studied and results obtained are given in Table XI.

Glasses in this system were easier to fiberize than those in the SiO_2-Al_2O_3-K_2O system, and ran at lower temperatures. However, most glasses devitrified readily. Also, they behaved in a peculiar manner, in that fibers of the sizes normally used for testing could be produced only by substantially reducing the pulling speed (2,000 vs. 3,600 rpm for a 6" diameter wheel). Normally, as the temperature is raised, the fiber diameter increases. With these glasses, raising the temperature increased the fiber diameter very little, up to the point at which the forming cone became too unstable to permit production of uniform fibers. Two possible reasons for this behavior suggested themselves: (1) these glasses might have an usually flat viscosity curve, that is, one in which viscosity changes relatively slowly with temperature; or (2) there might be an usual surface tension effect.

To check these possibilites, viscosity measurements were made on several of the glasses. Results are presented in Figure 11. It would be desirable to run softening points (log_η -7.6) to extend the length of the curves to determine their slopes more accurately. However, the ease with which these glasses devitrified made all attempts to do so unsuccessful   except for glass X-2083, which had a softening point of 1160°F. Inspection of all the available viscosity data suggests that these glasses have curves with about the slope that would be expected, and that this does not account for their forming behavior. A recent paper[5] indicates that that the lithium ion increases surface tension of glasses compared to the sodium and potassium ions. Perhaps this is related to the unusual forming behavior.

Forming temperatures reported do not very accurately reflect

TABLE XI
Compositions and Properties of Silica-Alumina-Lithia Glasses

Glass #	X-2075	X-2076	X-2077	X-2078	X-2079	X-2080	X-2081	X-2106	X-2107
Composition									
Mole % SiO_2	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00	75.00
Al_2O_3	-	3.13	6.25	9.38	12.50	15.00	16.25	17.50	18.75
Li_2O	25.00	21.88	18.75	15.63	12.50	10.10	8.75	7.50	6.25
Ave. Tensile Strength x 10^{-3}, psi	270	315	340*	428*	455*	527*	561*	612*	666*
Ave. Modulus x 10^{-3}, psi	9.38	10.05	10.38	10.52	10.47	11.37	11.70	11.95	12.20
Forming Temp. °F	2265	2505	2850*	3155*	3230*	3105*	3040*	2975*	3095*
Liquidus, °F	-	-	1890	-	-	-	-	-	-

Glass #	X-2082	X-2083	X-2084	X-2085	X-2086	X-2087	X-2088
Composition							
Mole % SiO_2	66.00	66.00	66.00	66.00	66.00	66.00	66.00
Al_2O_3	-	6.00	12.00	17.00	20.00	22.00	24.00
Li_2O	34.00	28.00	22.00	17.00	14.00	12.00	10.00
Ave. Tensile Strength x 10^{-3} psi	274*	293*	325*	370*	415*	465*	512*
Ave. Modulus x 10^{-3}, psi	10.06	10.46	10.80	10.59	11.20	11.60	11.96
Forming Temp. °F	1955*	2125*	2445*	2850*	2810*	2915*	3095*
Liquidus, °F	1893	1840	2120	2610	2550	-	-

| Glass #	X-2089	X-2090	X-2091	X-2092	X-2093	X-2094	X-2095	X-2096
Composition								
Mole % SiO_2	57.00	57.00	57.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	-	6.00	12.00	17.00	21.50	24.50	27.50	30.50
Li_2O	43.00	37.00	31.00	26.00	21.50	18.50	15.50	12.50
Ave. Tensile Strength x 10^{-3} psi	Could not run	Could not run	259*	319*	448*	367*	Could not run	Could not run
Ave. Modulus x 10^{-3}, psi	"	"	10.13	10.40	10.28	11.30	11.73	"
Forming Temp °F	-	-	2075*	2445*	2560*	2505*	-	-
Liquidus, °F	2145	2027	1905	2385	2587	2530	-	-

*Run at speeds lower than usual
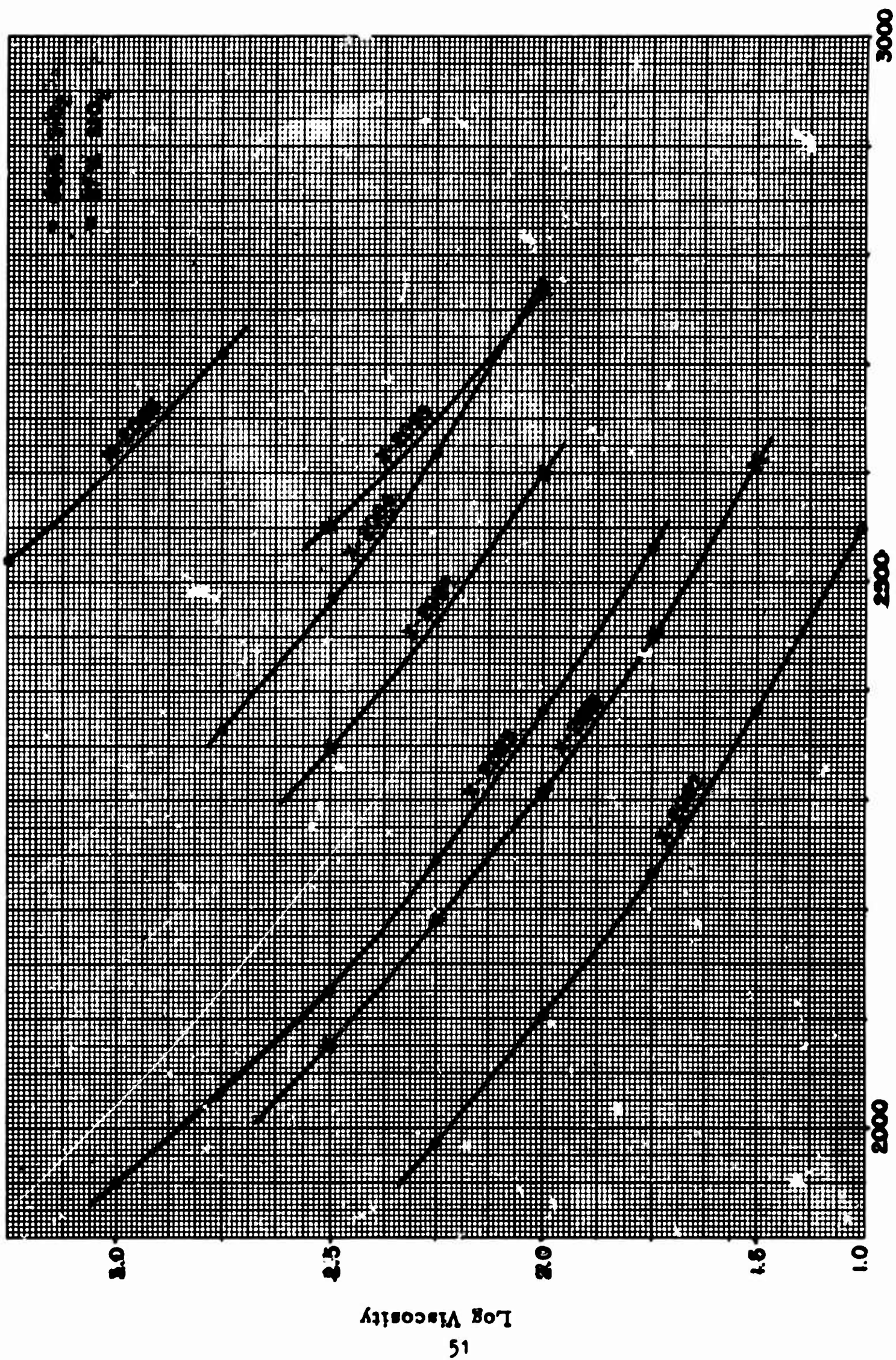
Figure 11 Log Viscosity Vs. Temperature For Glasses In The SiO_2-Al_2O_3-Li_2O System

differences in viscosity between glasses, because of the previously discussed relationship between forming temperature and fiber diameter. They do indicate a break at or near an Al/Li ratio of 1.0, such as that found for the other alkalis. The values obtained for glasses with the higher Al/Li ratios are the most uncertain because they were run at temperatures selected to prevent devitrification rather than to give the optimum viscosity.

There is no clear indication of a break in the tensile strength vs. composition curve at an Al/Li ratio of 1.0. Tensile strengths are rather higher for the lithia glasses than for the corresponding soda and potash glasses.

In view of the observed tendency of these glasses to devitrify readily, it was felt that knowledge of the relationship between liquidus and forming temperature might help explain the different behavior of these glasses compared to the corresponding soda and potash glasses. This difference was apparent both in forming behavior and in the failure to show a definite break in the tensile strength vs. composition curve. Accordingly, attempts were made to measure liquidus on most of these glasses. Liquidus is most conveniently measured by the so-called gradient boat method. Crushed glass is put in a long shallow platinum boat, which is introduced into a furnace constructed so as to have a nearly linear temperature gradient. The boat is left in the furnace for a time sufficient to permit the formation of devitrification, then withdrawn and quickly quenched in air. If the gradient was properly chosen, the boat will contain a region of clear glass and a boundary below which crystalline material may be found. The temperature pertaining to this boundary may be determined from the temperature distribution in the furnace. When this technique was applied to the lithia glasses, it was noted that the clear glass above the boundary devitrified during cooling. This process could not be completely stopped even by quenching the boat in water. Consequently, the boundary was estimated visually on the glass in the hot boat immediately after it was removed from the furnace. This Procedure could not be very accurate. However, results checked well with available data reported in the literature, which were obtained by the more accurate but more tedious quenching technique. Results are included in Table XI (Page 50). In most cases, the liquidus was well below the forming temperature, so that results should not have been affected by devitrification during forming. In a few cases, particularly at the 57% SiO_2 level, forming temperatures were barely over the liquidus. Results for these glasses might be questionable in view of the relative inaccuracy of liquidus and forming temperature measurements. However, they seem to be consistent with measurements in the other series and other systems.

Modulus is plotted as a function of composition in Figure 12. A break at an Al/Li ratio of 1.0 is clearly indicated. It is noteworthy that the curves do not fall in the same order as
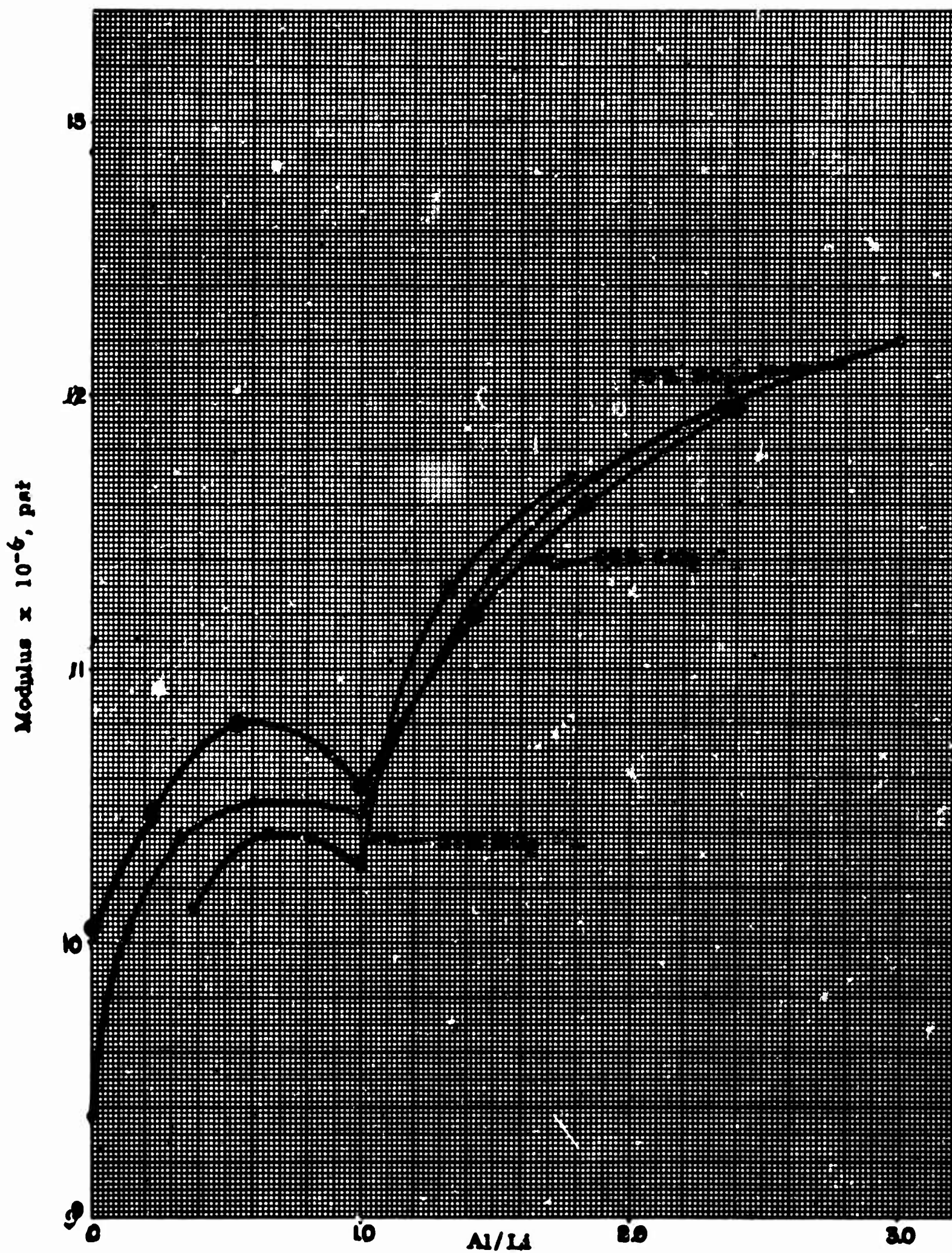
52

Figure 12 Modulus Vs. Al/Li Ratio

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SiO_2 contents and that they cross above an Al/Li ratio of 1.0.
Figure 13 shows the same data with modulus plotted as a function
of the ratio of Si plus Al to O. Again, two breaks are found,
one at 0.5, the other near 0.475. The lithia glasses clearly
show higher moduli than the corresponding soda or potash
glasses.

Because of the uncertainty of the glass viscosity measurement
as indicated by forming temperatures, and because of the
failure to find breaks in the tensile strength vs. composition
curves, density was run on these glasses. It was hoped that
density vs. composition curves would show a break at an Al/Li
ratio of 1.0, thus tending to corroborate the conclusions
that might be drawn from the breaks in the modulus vs. compo-
sition curves.   The data obtained are plotted in Figure 14.
The curves are drawn to the average values for several
determinations. The spread in results for each point is in-
dicated by the lengths of the vertical bars. The results
clearly indicate that a break exists at all three silica
levels in the curve of density vs. the Al/Li ratio at a
value of 1.0. This corroborates the finding on modulus.

c. SiO_2-Al_2O_3-K_2O-Li_2O System

The properties of the glasses containing Na_2O were inter-
mediate between those of the K_2O and Li_2O glasses, a not un-
expected result. It seemed likely that the properties of Na_2O
glasses could be duplicated by mixtures of Li_2O and K_2O at
comparable ratios of alkali ions to the other ions. It was
hoped that something could be learned regarding the role of
the alkali ions themselves by doing this.

Table XII gives results for a series of glasses in which the
ratio of ions selected corresponds to equal volumes of cations,
that is, the volume of the Li^+ plus K^+ ions equalled that of
an equal number of Na^+ ions. The compositions corresponde.
to the ones with Al/R ratios of one and the two nearest to
it for each SiO_2 level. Comparison of the data in Table XII
with results obtained on glasses containing Na_2O reveals that
the properties are obviously not a linear function of the
volume of the alkali cation.

Table XIII gives the results obtained on the second series
of glasses. These were selected on the basis of ionic field
strengths, using the relationship:

$$(1) \quad \frac{Li}{R^2_{Li}} + \frac{K}{R^2_K} \quad = \quad \frac{1}{R^2_{Na}}$$

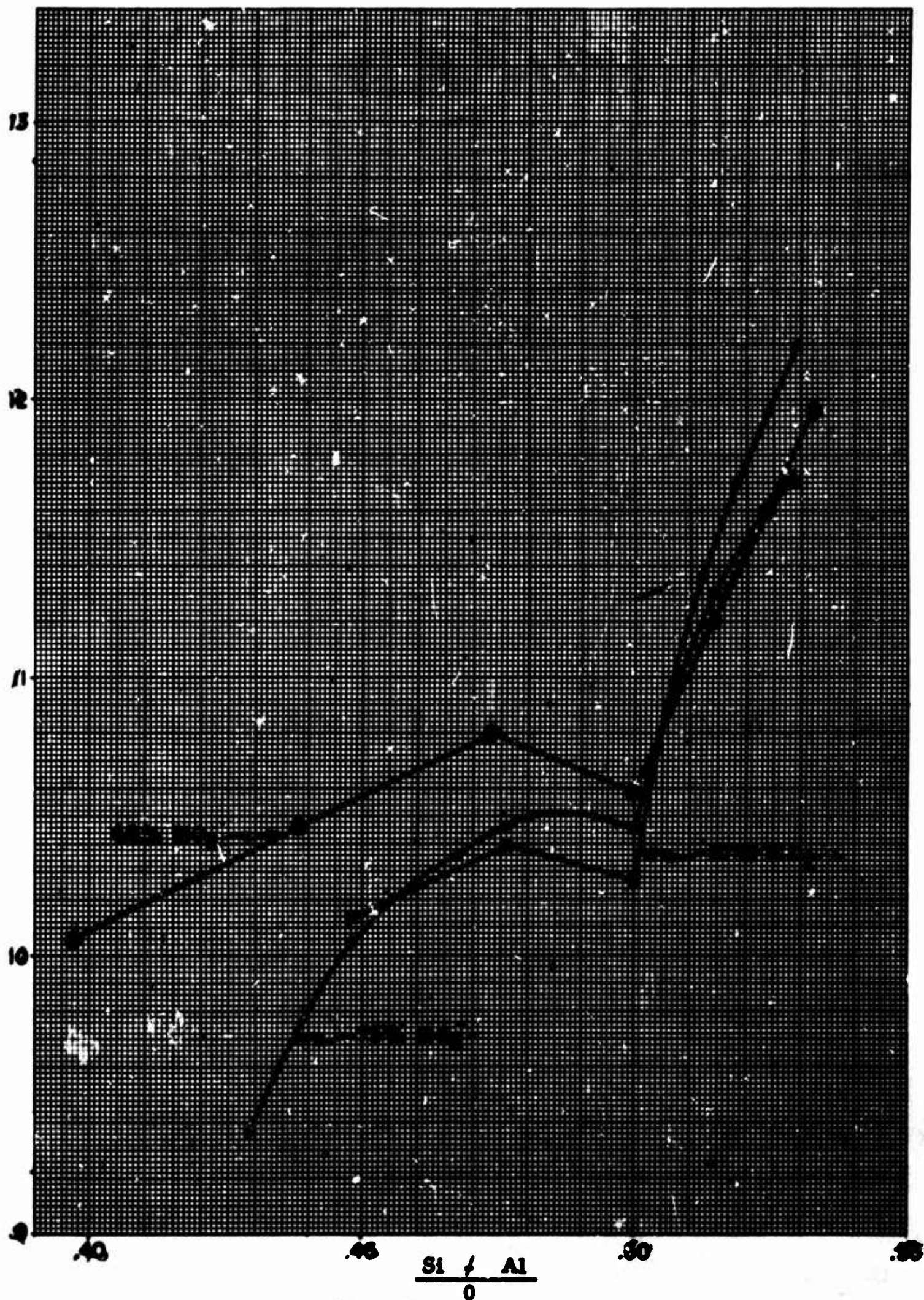where Li and K represent relative numbers of ions of lith-

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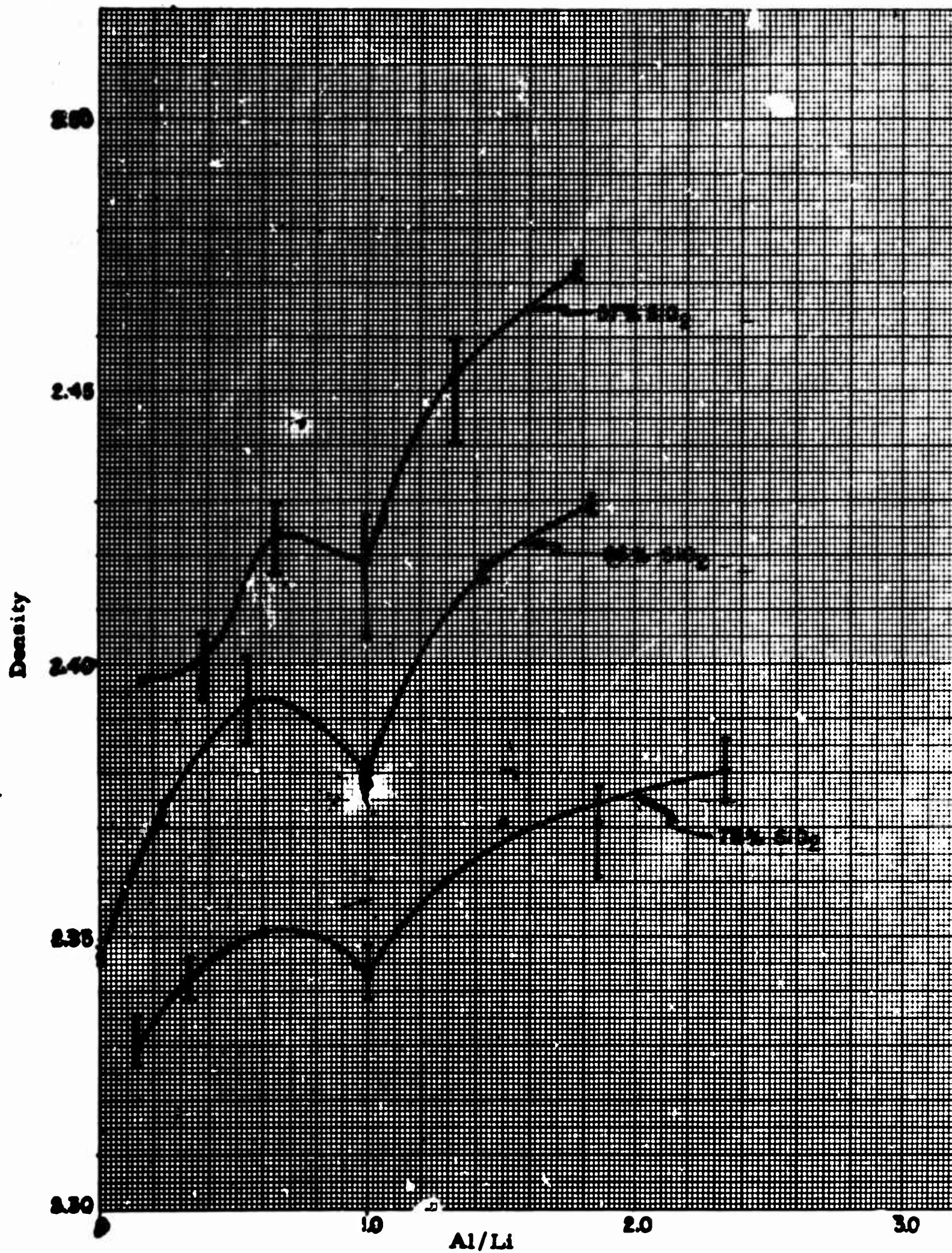Figure 13 Modulus Vs. $\frac{Si + Al}{0}$ Ratio For Glasses Containing Li_2O

Figure 14   .a-Lithia Glasses Density Vs. Composition

TABLE XII

COMPOSITION AND PROPERTIES OF
SILICA - ALUMINA - POTASH - LITHIA GLASSES
SERIES I

Glass #	X-2108	X-2109	X-2110	X-2111	X-2112	X-2113	X-2114	X-2115	X-2116
Composition									
Mole % SiO_2	75.00	75.00	75.00	66.00	66.00	66.00	57.00	57.00	57.00
Al_2O_3	9.38	12.50	15.00	12.00	17.00	20.00	17.00	21.50	24.50
K_2O	3.91	3.12	2.50	5.50	4.25	3.50	6.50	5.38	4.63
Li_2O	11.72	9.38	7.50	16.50	12.75	10.50	19.50	16.12	13.87
Modulus x 10^{-6}, psi	9.84	9.74	10.48	9.38 / 9.63*	8.98 / 9.54*	10.13 / 10.30*	10.32	10.15	11.10
Tensile Strength x 10^{-3}, psi	399	519	377	350	480	487	325	428	444
Forming Temperature °F, (2000 rpm)	3095	3115	3155	2530	2915	2975	2505	2645	2735
	Seedy	Seedy	Very Seedy (probably affected tensile strength)						

*Repeat

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TABLE XIII

COMPOSITION AND PROPERTIES OF
SILICA - ALUMINA - POTASH - LITHIA GLASSES
SERIES 2

Glass #	X-2143	X-2144	X-2145	X-2146	X-2147	X-2148	X-2149	X-2150	X-2151
Composition									
Mole % SiO_2	75.00	75.00	75.00	66.00	66.00	66.00	57.00	57.00	57.00
Al_2O_3	9.38	12.50	15.00	12.00	17.00	20.00	17.00	21.50	24.50
K_2O	10.50	8.41	6.73	14.80	11.44	9.42	17.49	14.47	12.45
Li_2O	5.12	4.09	3.27	7.20	5.56	4.58	8.51	7.03	6.05
Modulus, Average psi x 10^{-6}	9.02	8.73	9.58	9.43	9.42	10.03	9.26	9.45	9.95
Tensile Strength psi x 10^{-3}	418	N.D.*	N.D.*	343	372	427	334	443	416
Forming Temp. °F.	3060-3080	3250**	3250	2975	3040	3170	2975	3040	2915

*Not Determined

**Reduced Speed

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ium and potassium, the sum of which is 1.0. R is the ionic raduis of the indicated ion.

In general, the tensile strength of the glasses with mixed alkalis is near that of the lithia glasses, and among the higher values. It is difficult to generalize further about these data because of the scatter in results.

Data on forming temperatures were not plotted because they were not accurate enough reflections of viscosity to be meaningful. In general, they were consistent with the forming temperatures found for the other glasses.

Modulus data are plotted in Figures 15, 16, and 17. Figure 16 shows two sets of data for the mixed alkali glasses of Table XII. The second set, labeled "repeat" seems to fit better. It was obtained by rerunning the glasses after noting that the first set of data seemed inconsistent. Although the discrepancy is relatively small, it is greater than the error usually encountered. No explanation was apparent at the time the data were obtained.

The moduli of glasses in the second set, formulated on the basis of field strengths, lie rather close to those of the corresponding Na_2O glasses. However, they are consistently above the Na_2O curves. This led to an attempt to determine from the data the most likely ratio of K_2O to Li_2O to match the properties of Na_2O. Data were plotted to show the relationship between modulus and the proportions of Li_2O and K_2O for each SiO_2 level, and each ratio of aluminum to total alkali ions. There appears to be very nearly a straight line relationship between modulus and the Li/K ratio. Assuming a straight line relationship, the Li_2O-K_2O proportions that should give the same modulus as the corresponding Na_2O glass can be determined. The proportions of Li_2O and K_2O so determined vary quite widely from curve to curve. The precision of the data perhaps is not great enough for one to expect otherwise. However, there are enough data to suggest that an average value might be meaningful. On the average, mixtures of Li_2O and K_2O simulate the effect of Na_2O at the point at which the proportion of Li_2O is 21.7% of the total alkali.

Attempts to relate the average value for the point of intersection of the curves with ionic sizes are complicated by the precision with which ionic radii are known. For example, Table XIV gives ionic radii computed by four investigators for lithium, sodium, and potassium ions. For laying out the ratios of Li_2O to K_2O used in the series of mixed alkali glasses studied, average values were used. When these are used, equation (1) gives a value of 33% for the proportion of lithia. This is significantly higher than the average value
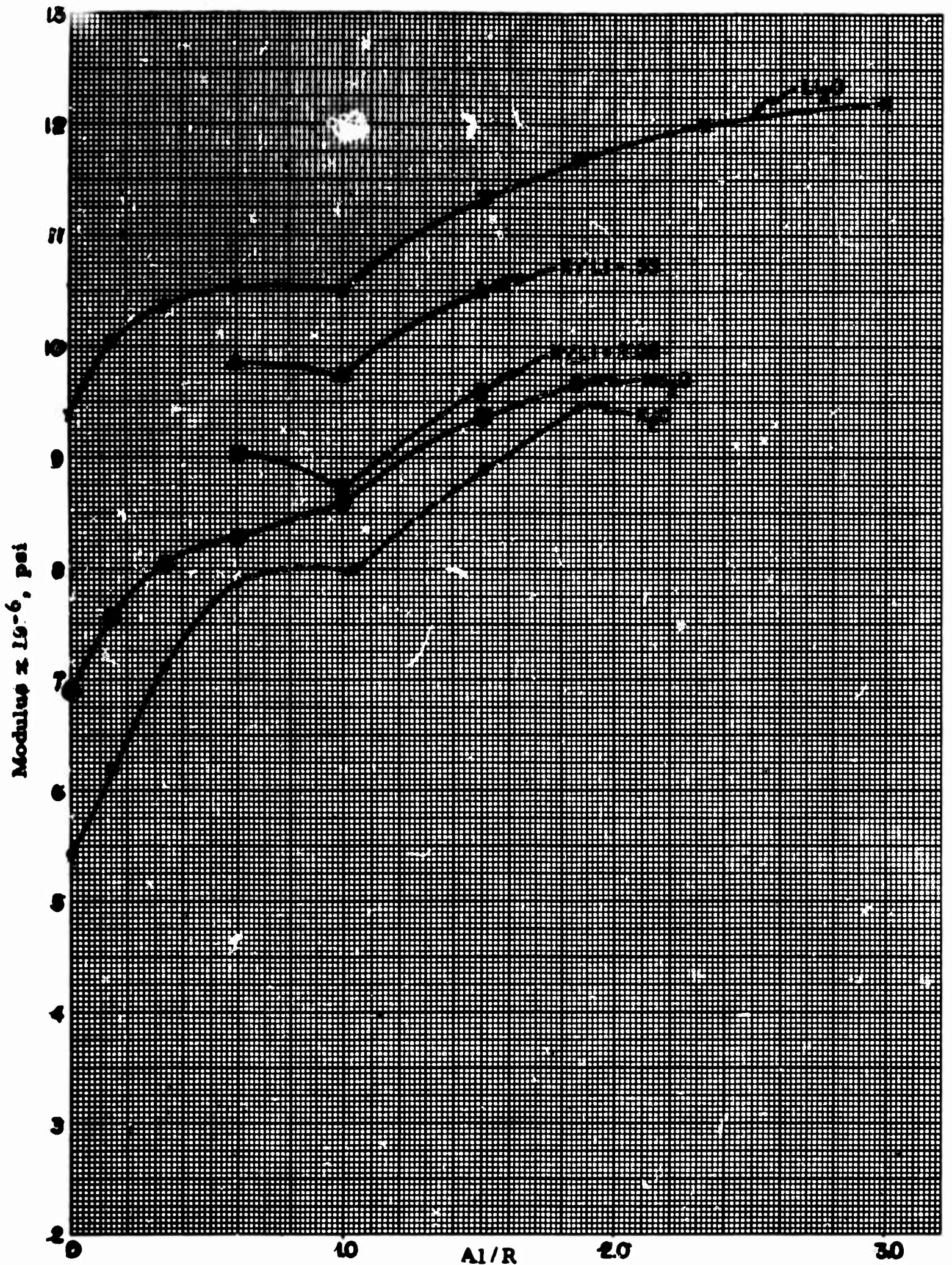
Figure 15 Silica-Alumina-Potash-Lithia Glasses Modulus Vs. Al/R Ratio at 75% SiO_2
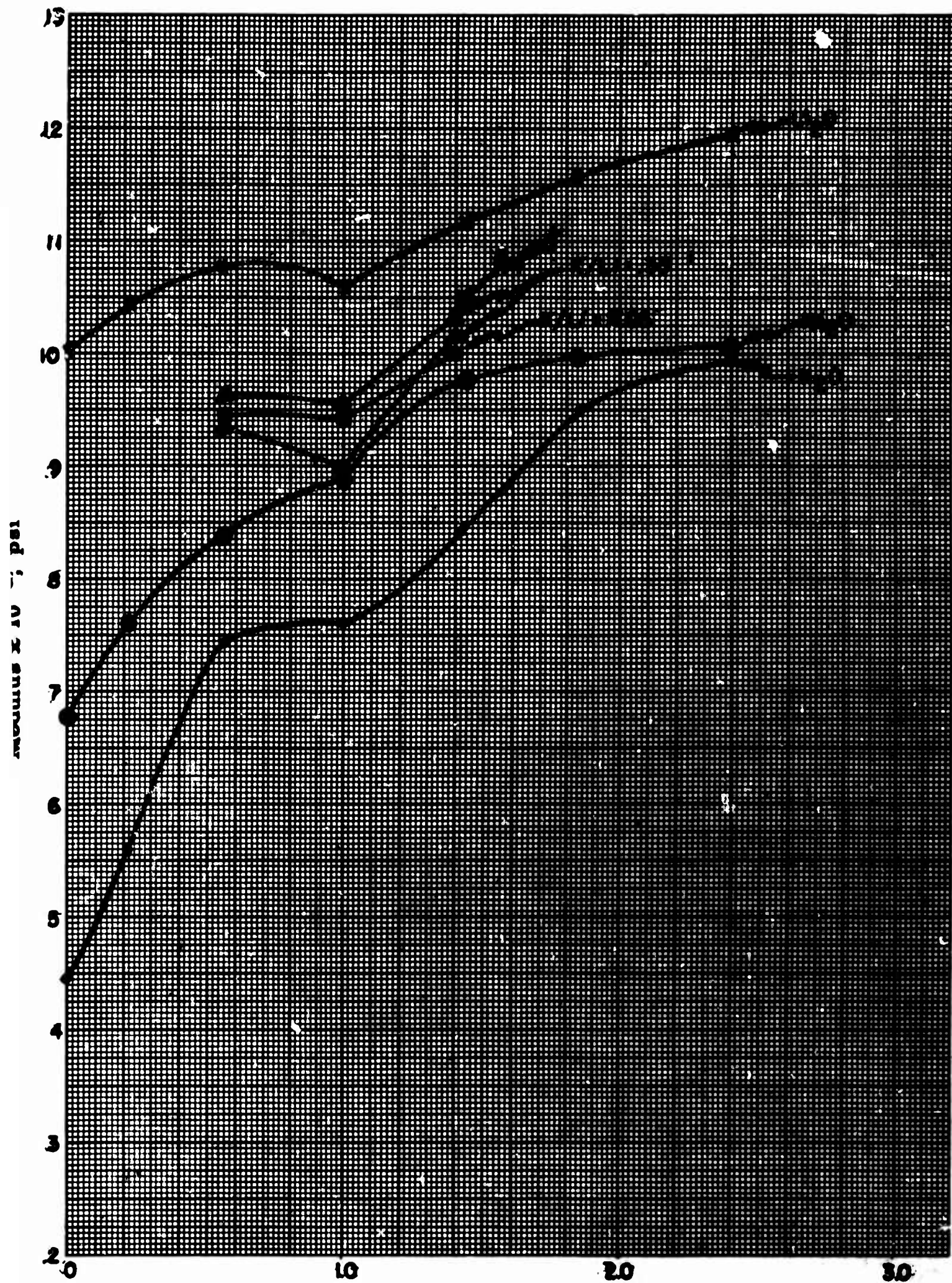
60

Figure 16 Silica-Alumina-Potash-Lithia Glasses Modulus Vs. Al/R Ratio at 66% SiO_2
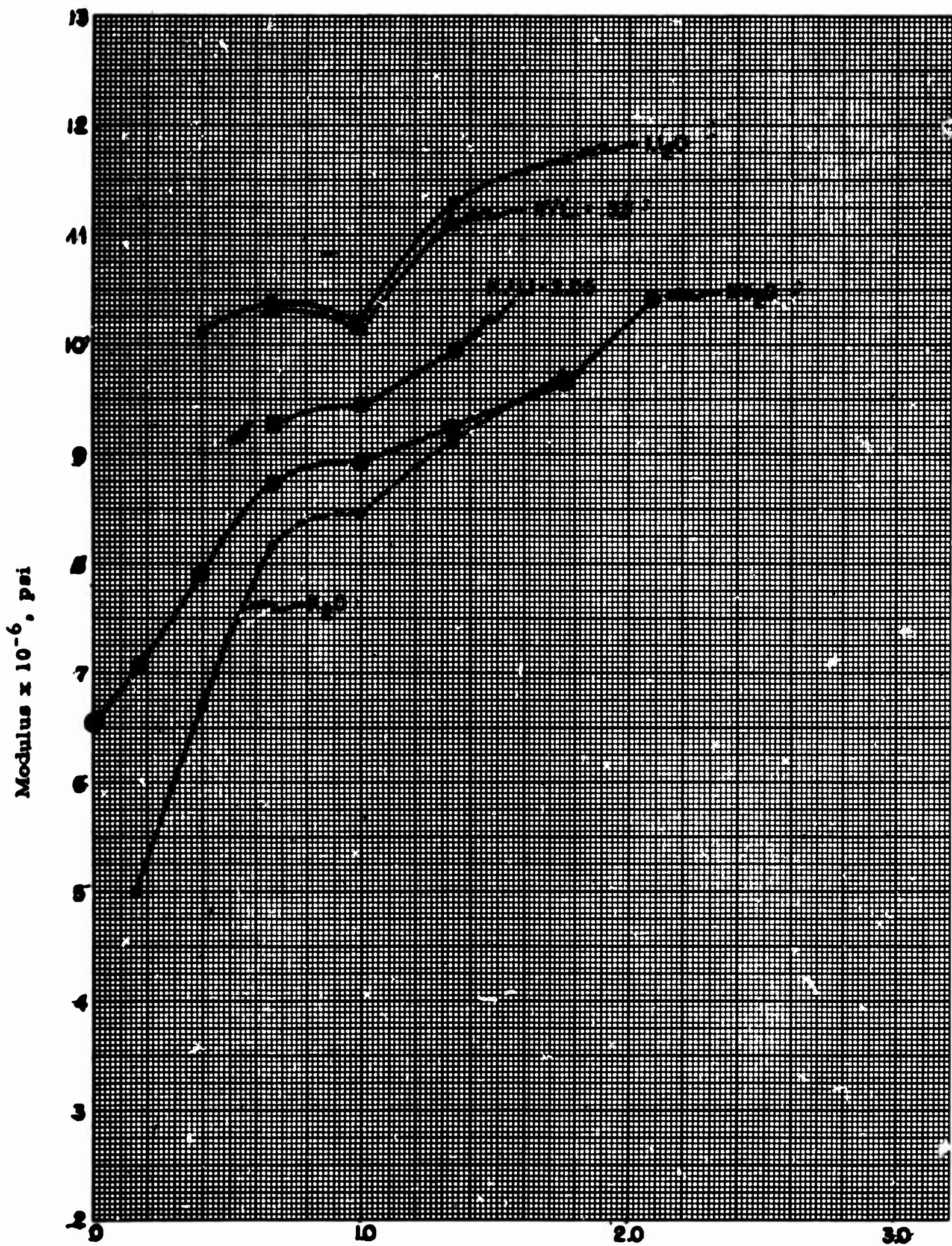
Figure 17 Silica-Alumina-Potash-Lithia Glasses Modulus Vs. Al/R Ratio at 57% SiO$_2$

of 21.7% obtained from the curves. Inspection of equation (1) shows that the value for the proportion of Li_2O would drop if powers of the ionic radius higher than two were used. For the fourth power, Li_2O would amount to 20.1% of the alkali, a rather good correlation with the value of 21.7% picked from the curves. On the other hand, if the ionic radii proposed by Pauling are used, equation (1) gives a value of 24.6% Li_2O, which also is fairly close to the average observed value of 21.7%. Thus, the data from both the current

TABLE XIV

IONIC RADII

Source	Li^+	Na^+	K^+
Goldschmidt	.78	.98	1.33
Pauling	.60	.95	1.33
Abrens	.68	.94	1.33
Zachariasen	.68	.98	1.33
Average	.685	.962	1.33

work and from work involving determination of ionic radii appear to be to inaccurate to permit establishing with certainty a valid relationship between ionic radii of the cations and modulus of elasticity, if an exists.

d. SiO_2-Al_2O_3-MgO System

Three series of compositions in the SiO_2-Al_2O_3-MgO system were formulated and tested. Most of these glasses were made up to have the same mole percentages as glasses previously studied except that MgO was substituted for the Group 1 oxides. One mole of MgO is equivalent to one mole of Group 1 oxides in that it introduces the same amount of oxygen. Therefore, the same mole percentages were selected for study in spite of the difference in valence of the added cation.

The compositions prepared and the properties obtained are listed in Table XV.

Beyond a general tendency for the higher silica glasses to be stronger, there does not appear to be a meaningful relationship between composition and tensile strength. It is felt that fiber forming difficulties caused the production of fibers so variable in quality that any relationship that might exist could not be found. Some glasses were not run at the optimum viscosity because of bushing temperature limitations. Others devitrified very readily at the optimum viscosity and were run at higher temperatures than normal. Some were probably actually fiberized below the liquidus.

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TABLE XV

Compositions and Properties of SiO_2-Al_2O_3-MgO Glasses

Glass #	X-2374	X-2369	X-2287	X-2200	X-2201	X-2286	X-2202
Composition							
Mole % SiO_2	75.00	75.00	75.00	75.00	75.00	75.00	75.00
Al_2O_3	4.20	5.25	6.25	9.38	12.50	13.40	15.00
MgO	20.80	19.75	18.75	15.63	12.50	11.10	10.00
Ave. Tensile Strength x 10^{-3} psi	512	N. D.	434	630	568	611	609
Ave. Modulus x 10^{-6}, psi	12.22	12.08	11.60, 11.82 11.82, 12.16	12.00 11.98	12.40	12.62	12.94
Forming Temp °F	3215	3155	3095	3215	3095	3075	3060

Glass #	X-2289	X-2373	X-2203	X-2372	X-2204	X-2288	X-2205
Composition							
Mole % SiO_2	66.00	66.00	66.00	66.00	66.00	66.00	66.00
Al_2O_3	6.00	9.71	12.00	14.57	17.00	18.90	20.00
MgO	28.00	24.29	22.00	19.43	17.00	15.10	14.00
Ave. Tensile Strength x 10^{-3} psi	525	N. D.	525	N. D.	468	515	449
Ave. Modulus x 10^{-6}, psi	12.84 12.88	12.63	12.48 12.52	12.80	12.82 12.95	12.95 13.22	13.50 13.66
Forming Temp °F	2830	2770	3020	2975	2875	2770	3095

Glass #	X-2291	X-2376	X-2206	X-2375	X-2207	X-2290	X-2208
Composition							
Mole % SiO_2	57.00	57.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	12.00	14.90	17.00	19.10	21.50	23.00	24.50
MgO	31.00	28.10	26.00	23.90	21.50	20.00	18.50
Ave. Tensile Strength x 10^{-3} psi	541	545	510	494	430	Could not form test fibers	
Ave. Modulus x 10^{-6}, psi	13.86 14.00	13.50	13.20 13.08	13.42	13.56	13.82	14.26
Forming Temp. °F	2505	2585	2735	2560	2850	2735	2975

The difficulty of forming fibers also made it impractical to relate composition with viscosity as shown by forming temperatures. In addition, there was a change of bushings during the series, resulting in an abrupt change in bushing temperature readings, probably as a result of the drift in reading of the older thermocouple.

The preparation of fibers suitable for modulus measurement is less difficult than the preparation of good fibers for tensile strength tests. As far as is known, fiber modulus is not greatly affected by forming difficulties, so long as seeds and crystalline material do not appear in the fibers. Therefore, it seems probable that the results obtained on the modulus measurements are valid within the limitations of the measurement as described later. Results are shown graphically in Figure 7 (Page 33). Note that modulus is plotted vs. 2 Al/Mg. On the basis of the oxygen available for coordination with the silicon and aluminum ions, this ratio is equivalent to the ratio Al/Na' used on the first series of glasses studied. It is apparent that results for this system are far different from those for Group 1 alkalis. It is possible that there is an inflection of the curves at the point where the 2 Al/Mg ratio is one, but it is very small if present at all. However, there is a marked break in the curves at some lower ratio. The location of the break varies with the silica content, being at a lower value for the higher silica levels. When modulus is plotted vs. $(Si + Al)/O$, the curves resemble those for modulus vs. 2 Al/Mg. They do not show inflections at either 0.5 or 0.475 as did the curves for glasses containing Group 1 oxides.

Density measurements were made on most of the MgO glasses in an effort to find another property which showed breaks when plotted against composition similar to those found in the modulus vs. composition curves. Results are shown in Figure 16. It is apparent that density changes very little as the 2 Al/Mg ratio changes. The spread in results is great enough to mask any effects that might be present, although there appears to be an inflection at the 57% SiO_2 level corresponding to that found for modulus. It would be possible to reduce the experimental errors leading to the spread in results by greater care in all details starting with the preparation of the glass. However, it appears that any breaks that may exist would be so slight that even precise data would be rather inconclusive. Further work was therefore not done.

e. $SiO_2-Al_2O_3-CaO$ System

A number of glasses in this system were prepared to determine whether other oxides in Group 2 behave in a manner similar to magnesia. The compositions melted and results obtained are given in Table XVI.
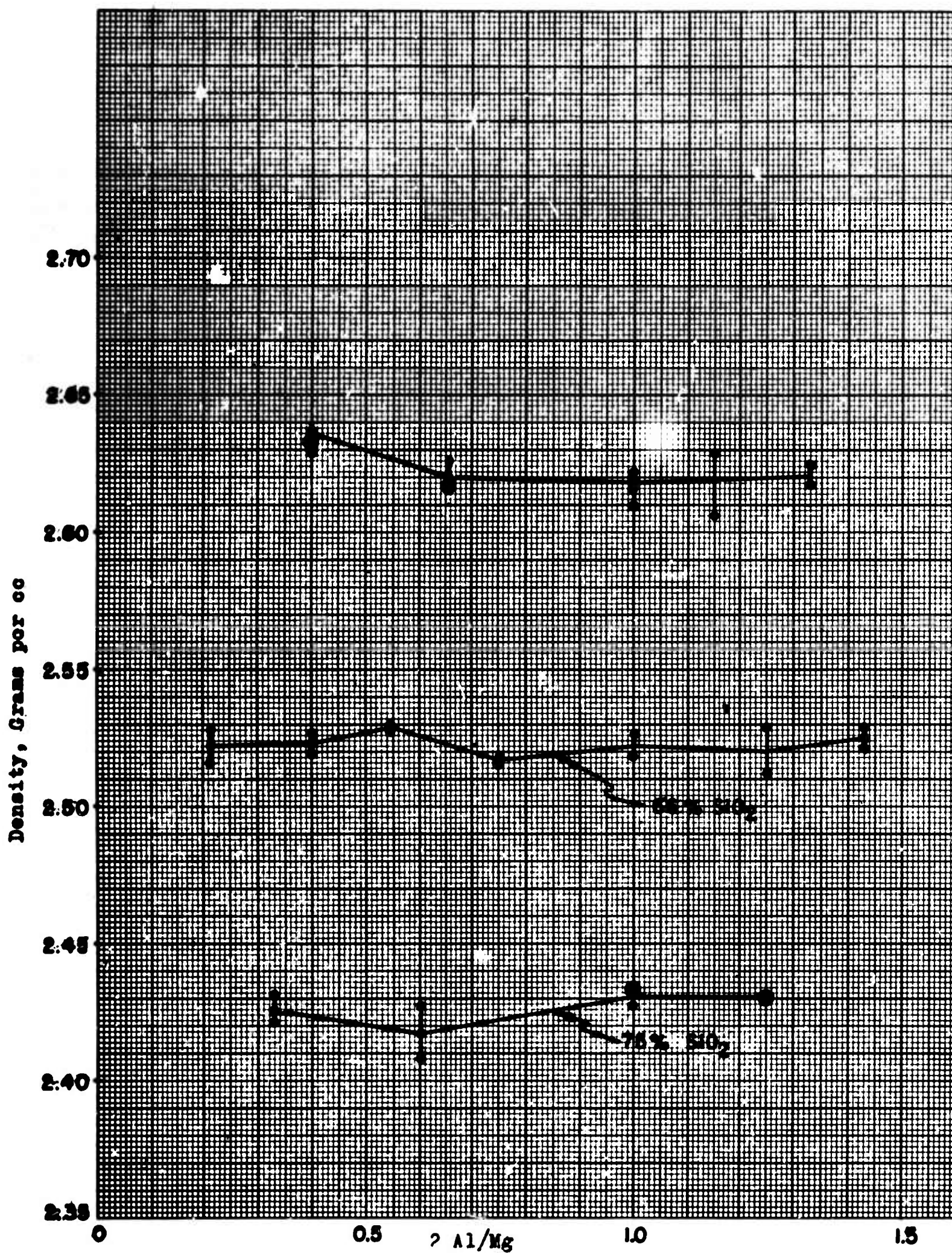
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Figure 18 Density Vs. 2 Al/Mg Ratio

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TABLE XVI

COMPOSITION AND PROPERTIES OF GLASSES IN THE SiO_2-Al_2O_3-CaO SYSTEM

Mole %	X-2315	X-2228	X-2229	X-2314	X-2230	X-2317
SiO_2	75.00	75.00	75.00	75.00	75.00	66.00
Al_2O_3	6.25	9.38	12.50	13.90	15.00	6.00
CaO	18.75	15.63	12.50	11.10	10.00	28.00
2 Al/Ca	.33	.60	1.00	1.25	1.50	.214
Modulus, Ave. x 10^{-6}, psi	11.30	11.10	10.92	11.28	11.50	12.20
Modulus, Recheck		11.30	11.02			
Tensile Strength x 10^{-3}, psi	478	215	274	348	457	357
Tensile Strength, Recheck		370	524			
Forming Temp, °F	3105	3215	3215	3215	3215	2645

	X-2231	X-2232	X-2316	X-2233	X-2319	X-2234	X-2235	X-2318	X-2236
Mole %									
SiO_2	66.00	66.00	66.00	66.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	12.00	17.00	18.90	20.00	12.00	17.00	21.50	23.00	24.50
CaO	22.00	17.00	15.10	14.00	31.00	26.00	21.50	20.00	18.50
2 Al/Ca	.545	1.00	1.25	1.43	.397	.654	1.00	1.15	1.324
Modulus, Ave. x 10^{-6}, psi	12.40	12.22	12.62	12.96	12.22	12.88	12.76	13.10	13.40
Tensile Strength x 10^{-3}, psi	362	423	492	543	326	416	475	414	511
Forming Temp, °F	2890	2955	2953	3000	2480	2735	2745	2795	2770
						Slight Devit.	Slight Devit.		Slight Devit.

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A rather striking example of the dependence of tensile strength on the thermal history of the glass was observed. While running the center three members of each series, an unexpected result was obtained in that the glasses with the highest SiO_2 contents appeared to give the lowest strengths. When additional glasses were run, the first glass in the 75% SiO_2 series gave results higher than the others, which made the first results seem out of line. Two of the compositions were remelted for 24 hours at 2900°F. These conditions had earlier been found to give improved strengths with other glasses as reported in Section II. This melting treatment resulted in marked increases in the tensile strengths as indicated by the values for the tensile strength rechecks in Table XVI. There still appears to be a dip in the curve for the 75% SiO_2 level at a 2 Al/Ca ratio of 0.6. However, results were too erratic to justify the conclusion that this was significant. Rather, it was concluded that the tensile strengths actually measured showed dependence upon thermal history great enough to mask any effects caused by glass structure changes resulting from glass compositon alone.

Modulus is plotted vs. composition in Figure 19. There is definitely an inflection in the curves at the point where the 2 Al/Ca ratio is one. The curves were not extended over as large a composition range as was done for most of the series containing Group 1 oxides because of forming difficulties. However, enough points were obtained to show that the curves for the calcia glasses resemble those for the glasses containing Group 1 oxides, and that they do not resemule the curves for the series of glasses containing magnesia. Modulus values are higher, however, than those for the glasses containing the Group 1 oxides. In this, the calcia series is more similar to the magnesia series.

f. $SiO_2-Al_2O_3-ZnO$ System

The unique results obtained for the modulus vs. composition relationship with the glasses containing MgO suggested that it would be interesting to study a similar system with ZnO replacing MgO.

The valence and ionic radii of zinc and magnesium are similar. The compositions studied and the results obtained are given in Table XVII.

Tensile strength and forming temperature data are not very reliable because of the difficulty associated with the forming of suitable fibers.

Modulus is plotted vs. composition in Figure 4 (Page 9). The curves are rather similar to those found for the MgO series of glasses. There is no clear indication of an inflection at the point where the 2 Al/Zn ratio is one. There is an inflec-
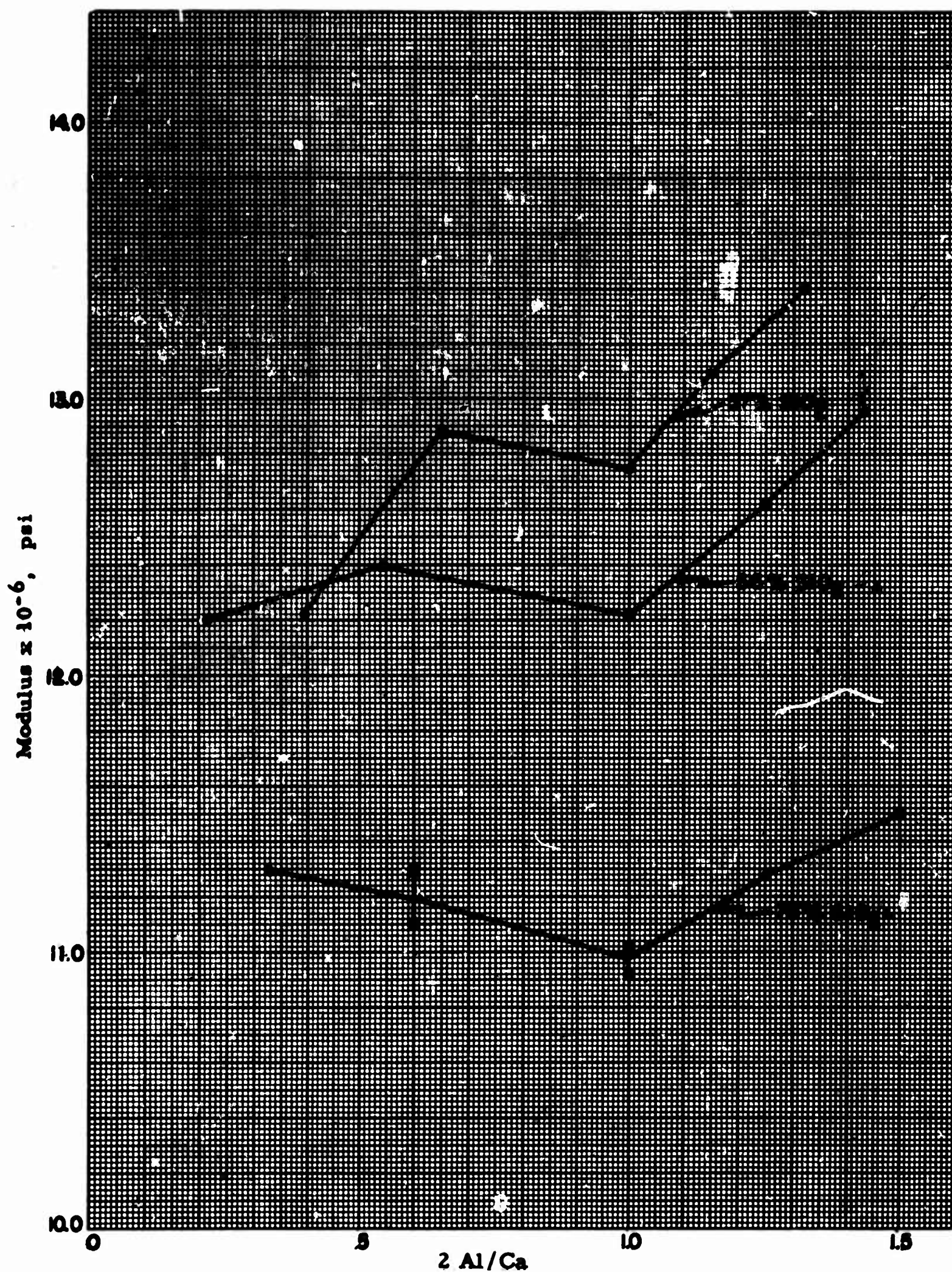
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Figure 19   Modulus Vs. 2Al/Ca Ratio for Silica-Alumina-Calcia Glasses

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TABLE XVII

Compositions and Properties of SiO_2-Al_2O_3-ZnO Glasses

Glass #	X-2386	X-2385	X-2360	X-2361	X-2362
Composition					
Mole % SiO_2	75.00	75.00	75.00	75.00	75.00
Al_2O_3	4.20	6.25	9.38	12.50	15.00
ZnO	20.80	18.75	15.63	12.50	10.00
Ave. Tensile Strength x 10^{-3} psi	482	459	469	609	622
Ave. Modulus 10^{-6}, psi	11.62	11.26	11.66	11.78	12.38
Forming Temp, °F	3150	3215	3215	3155	3040

Glass	X-2382	X-2381	X-2363	X-2380	X-2364	X-2365
Composition						
Mole % SiO_2	66.00	66.00	66.00	66.00	66.00	66.00
Al_2O_3	6.00	9.71	12.00	14.57	17.00	20.00
ZnO	28.00	24.29	22.00	19.43	17.00	14.00
Ave. Tensile Strength x 10^{-3} psi	N.D.	508	446	530	492	641
Ave. Modulus 10^{-6}, psi	13.58	13.22	12.80	12.90	13.15	13.96
Forming Temp. °F	- Fibers opal.	2620	2850	2700	2850	3155 Devit.

Glass #	X-2387	X-2388	X-2366	X-2389	X-2367	X-2368
Composition						
Mole % SiO_2	57.00	57.00	57.00	57.00	57.00	57.00
Al_2O_3	12.00	14.90	17.00	19.10	21.50	24.50
ZnO	31.00	28.10	26.00	23.90	21.50	18.50
Ave. Tensile Strength x 10^{-3} psi	418	567	408	545	N.D.	441
Ave. Modulus 10^{-6}, psi	13.64	13.56	13.50	13.60	13.83	14.62
Forming Temp. °F	2570	2505 Devit.	2680 Devit.	2610 Devit.	3050 Devit.	2850 Devit.

tion in all curves at some lower value. The inflection points correspond to those found in the MgO system.

4. Discussion of Results

Of all the data obtained, modulus measurements appear to be the most valuable. Tensile strength and fiber forming temperatures appear to be quite useful in the earlier study of the glasses containing Na_2O. Most of the glasses in that system ran well at attainable temperatures and required no special fiber forming techniques. The reliability of tensile strength and forming temperature data became less for the K_2O and Li_2O containing glasses because of the high forming temperatures of the former and the high devitrification rate and peculiar forming behavior of the latter. Difficulties in getting good data became even greater for the glasses containing divalent ions. Many of these glasses had to be run at the maximum safe temperature of the bushing, and even there perhaps at reduced speeds. Under these conditions, it is not likely that the glass can be conditioned to produce fibers of optimum strength, or that the fiber forming conditions themselves can be optimum. There is no opportunity for adjusting forming variables so as to find the conditions which produce optimum strengths. Other glasses devitrify so readily that they must be formed at the opposite boundary conditions for fiber formation, and here again no opportunity exists to change variables to determine optimum strengths. The measurement of tensile strengths under these conditions appeared justified for two reasons:

a. It could not be known in advance how many glasses in a series would have to be formed under conditions such that strength values would not be near enough to the optimum to permit valid comparisons.

b. Even non-optimum values might uncover areas of particular interest which would warrant more extensive investigation.

Certain of the variables associated with measuring forming temperature, such as drift in thermocouple EMF with aging or differences between bushings could have been taken account of and compensated for by known techniques. This was not done for two reasons:

a. So many of the glasses had to be fiberized by resorting to arbitrary adjustments in temperature and pulling speed that useful comparisons between glasses would still not have been possible.

b. Forming temperatures were of secondary interest, and were noted principally in the hope that they might serve as an additional variable sensitive to glass structure which might be used to corroborate conclusions drawn from modulus or strength measurements.

The modulus of elasticity seems to be relatively insensitive

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to forming variables. Values obtained on fibers drawn with
difficulty seemed generally to fall in line with results from
more easily fiberized glasses provided only that the fibers
were not hollow and did not contain crystalline inclusions.
The spread in results for a given set of modulus determinations
(ten measurements on five fibers) rarely exceed 0.3×10^6 psi.
On several occasions, a complete recheck of modulus measurements
was made, as indicated in the tables, particularly Table XV
(Page 64) which contains the data for the MgO series. Usually
these repeat measurements checked each other within 0.3×10^6 psi,
exactly. In some cases, the repeat measurements were made on
fibers produced from different bushings. The largest variation
was found for glass X-2267 (Table XV, Page 64) for which aver-
age values of 11.60, 11.82, 11.82, and 12.16 were obtained. The
total spread in average results here is 0.56×10^6 psi. This
does allow the possibility that differences in forming or testing
conditions could influence results by this much. However, the
variation was not related to any obvious difference in forming
conditions.

For these reasons it is felt that in this study modulus measure-
ments provided the most reliable and most valuable data for
correlating properties with glass structure. It is apparent that
for glasses containing the oxides Li_2O, Na_2O, K_2O and CaO,
additions of Al_2O_3 increases the modulus in a non-uniform manner.
The rate increase is relatively large with small additions,
becomes smaller or even negative with intermediate additions.
and increases again at still larger additions. The change
from small to larger rates of increase takes place where the
ratio of aluminum ions to alkali ions is one. This is con-
sistent with the theories of glass structure previously de-
veloped for the silica-alumina-soda glasses only. For in-
creasing the modulus of a glass the desirability of these
alkalis falls in the following order: CaO, Li_2O, Na_2O, and
K_2O. This is in line with the ionic strength of these ions.
Lithium, with its small radius, is the best of the Group 1
alkalis. The charge of two for the calcium ion explains its
position ahead of lithium, even though it is a large ion.

MgO and ZnO are nearly equivalent in effect and both are
superior to the other ions for increasing modulus. The ratio
of ionic charge to radius is higher for these ions than for
those in the preceding group. It is logical that these ions
should tend to tighten the glass structure and thus raise
the modulus. It is probable that these ions participate some-
what in the glass network. This is inferred from the observa-
tion that the modulus vs. composition curves do not show a
break at an aluminum to alkali ion ratio of one. These ions
apparently interfere with the change in coordination number
of the aluminum as oxygen is added, probably because they
tie up some of the oxygen themselves. That these ions may
possibly participate in the network itself has been postu-
lated by other investigations on the basis of other evidence.

Ainswotrh[6], for instance, discussed this possibility in connection with his work on the relaticnship between glass compositions and hardness. He also found an anomaly with magnesium and zinc oxides when comparing the effect various oxides had on the diamond pyramid hardness of glass. He noted a general tendency for certain oxides from Groups 1, 2, and 3 to increase the hardness of a base glass by amounts that seemed usually to be in the same order as ionic strengths. He found that magnesium and zinc oxides increased hardness rather less than expected on this basis, and postulated that this might be explained by some participation by these ions in the glass network. It is noteworthy that he found hese oxides rather less effective in increasing hardness than expected. Since hardness is likely to be related to modulus, this evidence seems to be contradictory to the findings of this study, which showed these oxides to be more effective than others in raising modulus. The explanation may lie in the base glass used. Ainsworth added the oxides studied to a base glass containing SiO_2 and Na_2O, while the base glass used in the current study contained SiO_2 and Al_2O_3.

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13. ABSTRACT

The purpose of this investigation has been the study of glass compositions capable of producing glass fibers having high tensile strength-high modulus of elasticity properties which are also low in density. Of the many compositions studied, those which have the best promise of meeting the required properties are located in the SiO_2-Al_2O_3-BeO system. In particular, compositions have been developed in this system with tensile strengths of 680-715,000 psi, moduli of 14-15 x 10^6 psi, and bulk densities of 2.41-2.50. These properties produce fibers with specific strengths and specific moduli in excess of any currently available glass fiber. Successful multifilament manufacture of glasses of this nature was demonstrated and unidirectional filament wound composites were fabricated and tested. In a basic study aimed at relating glass properties, composition, and structure, three and four component systems were studied consisting of SiO_2 and Al_2O_3 plus one of the following: K_2O, Li_2O, $K_2O + Li_2O$, MgO, CaO, ZnO and BeO. For glasses containing K_2O, Li_2O, $K_2O + Li_2O$, or CaO, curves of modulus vs. the ratio of aluminum to added ion showed breaks at the point where one oxygen ion had been added per two aluminum ions. This was related to a proposed glass structure involving a change of coordination number of aluminum from four to six, with a corresponding change in the function of this ion in the structure. BeO, MgO and ZnO were similar to each other in behavior, but differed from the other oxides. They showed breaks in composition vs. modulus curves at different points than the other oxides, with the inflection point changing with SiO_2 content. These oxides increased modulus in the following order (BeO highest): BeO, MgO, ZnO, CaO, Li_2O, Na_2O, K_2O.

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